Influence of Natural Organic Matter and Mineral Colloids on Arsenic (As) and Uranium (U) Transport in Geological Media

by

© Qing Wang

A Thesis submitted to the

School of Graduate Studies

in partial fulfillment of the requirements for the degree of

Master of Science

Environmental Science Program

Memorial University of Newfoundland

May 2014

St. John's Newfoundland

ABSTRACT

Arsenic (As) and uranium (U) are two common groundwater contaminants that threaten human health. To assess the scope of As and U contamination in groundwater, it is important to characterize and quantify As and U migration in porous geo-media. This thesis research examined the influence of natural organic matter and mineral colloids on As and U transport. As and U transport was investigated by injecting As-spiked or U-spiked solution/suspension into water-saturated columns packed with natural sediments and quartz sand, and analyzing As or U concentration in column effluent. Column experiment results showed that natural organic matter substantially increased As and U transport, while mineral colloids had only minor effects on As and U transport. When natural organic matter and mineral colloids co-existed, As transport was lower, but U transport was higher compared to that in systems with HA but no illite.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor, Dr. Tao Cheng, for offering mentorship and fresh ideas throughout all stages during my study and research work. He showed me extraordinary understanding of research work and offered me encouragement and help whenever I needed.

I also extend thanks to Lakmali Hewa, Jamie Warren, Donna Jackman, and Wanda Aylward for their frequent help with analytical instruments and materials. In addition, thanks to Md. Samrat Alam for helping me in collecting samples and cheerful talking when I felt depressed.

I also gratefully acknowledge financial support from the Research & Development Corporation of Newfoundland and Labrador's Ignite R&D Program and School of Graduate Studies Fellowship provided by Memorial University of Newfoundland.

And of course I would like to thank my family for their support in my study and research. Their love is the most powerful backing to me.

Table of Contents

List of Tables

List of Figures

Nomenclature

Al – aluminium

As – arsenic

cm – centimeter

cm/min – centimeter per minute

cm^3 – cubic centimeter

Eh – oxidation/reduction potential

Fe – iron

g – gram

g/cm^3 – grams per cubic centimeter

HA – humic acid

HS – humic substance

ICP-MS – inductively coupled plasma mass spectrometry

kg – kilogram

L – liter

M – mole

MAC – maximum acceptable concentration

mg – milligram

ml – milliliter

mg/kg – milligrams per kilogram

mg/L –milligrams per liter

mm – millimeter

mol/L – moles per liter

nm – nanometer

NOM – natural organic matter

pH – power of hydrogen; a measure of hydrogen ion activity

pH_{pzc} – point of zero charge

pK_a – logarithmic acid dissociation constant

U – uranium

WHO – World Health Organization

XRD – X-ray diffraction

℃ – Degree Celsius

μg – microgram

μg/L – micrograms per liter

μm – micrometer

Chapter 1. Introduction and Overview

Natural organic matter (NOM) and mineral colloids are ubiquitous in groundwater and the vadose zone. Due to large surface area and abundance of surface functional groups, NOM and mineral colloids strongly adsorb many aqueous contaminants. NOM and mineral colloids are highly mobile in subsurface environment, therefore the mobility of strongly sorbing contaminants can substantially increase when these contaminants are retained by NOM and mineral colloids. Colloid- and NOM-facilitated transport of heavy metals, radionuclides, and organic contaminants in subsurface environment have been extensively studied (Grolimund, et al., 1996; Tatalovich, et al., 2000; Schmitt, et al., 2003; Yang, et al., 2012). Arsenic (As) and uranium (U) are common contaminants in groundwater and their occurrence have been suggested to be related to the occurrence of NOM and mineral colloids (Betcher, et al., 1988; Baumann, et al., 2006; Guo, et al., 2009; Guo, et al., 2011). However, influence of NOM and mineral colloids, especially their combined effects on As and U transport, is not fully understood at this time. This gap in knowledge prevents us from accurately predicting the extent of As and U contamination in subsurface environments.

1.1 Natural occurrence, speciation, toxicity, and migration of arsenic in subsurface environment

Arsenic (As) is a naturally occurring element and ranks the 20th most abundant

element in the earth's crust (Mandal and Suzuki, 2002). Arsenic is found throughout rocks, soils, and natural waters (Wang and Mulligan, 2006). As a metalloid, arsenic is frequently referred to as a heavy metal in the context of toxicology (Mandal and Suzuki, 2002; Jomova, et al., 2011).

As concentration is usually low in surface water (lake and river), but in groundwater could be as high as 5000 μg/L under natural conditions (Smedley and Kinniburgh, 2002). High As concentration in groundwater is likely to be found in areas with high As content in bedrocks (Boyle, et al., 1998). As released due to reductive dissolution of Fe(III)-oxyhydroxides dominates the geochemical source of As in groundwater in some areas (Maity, et al., 2011). Elevated concentration of As is found in geothermal regions (Aiuppa, et al., 2006; Abbasnejad, et al., 2013) and alluvial aquifers (Ahmed, et al., 2004). Anthropogenic sources of arsenic contamination, such as industrial processes (e.g., mining and smelting), agricultural pesticides, and chemicals for wood protection enhances As contamination in the environment (Patel, et al., 2005; Dobran and Zagury, 2006; Akter and Ali, 2011).

As is mainly present as inorganic As(III) and As(V) in groundwater and As occurs in the environment in several oxidation states (-3, 0, +3, and +5) (Smedley and Kinniburgh, 2002). Aqueous speciation of As depends on pH and redox potential (Eh) (Smedley and Kinniburgh, 2002; Wang and Mulligan, 2006). Under oxidizing conditions, As(V) is dominant and present as $H_2AsO_4^-$ and $HAsO_4^{2-}$ with pK_a values of 2.2, 6.9, and 11.5; under reducing conditions, As(III) predominates as H_3AsO_3 with

pK_a values of 9.2, 12.7, and 13.4 (Fig. 1.1 & 1.2) (Smedley and Kinniburgh, 2002; Sharma, et al., 2011). As(V) and As(III) could co-exist and As(III) is more mobile and toxic than As(V) (Tufano and Fendorf, 2008; Sharma, et al., 2011). Organic forms of As are usually of less concern because of their low toxicity and low concentration in groundwater (Smedley and Kinniburgh, 2002).

The maximum acceptable concentration (MAC) of As in drinking water recommended by Health Canada and World Health Organization (WHO) is 10 μg/L (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002; Health Canada, 2006). Exposure to high level of As could cause a series of diseases to human. As is toxic to the majority of organs and the most sensitive organ is kidney (Cohen, et al., 2006). As exposure has been linked to cell damage, dermal diseases, various types of cancer, cardiovascular diseases, gastrointestinal disturbances, liver diseases, neurological disorders, and reproductive health effects (Jomova, et al., 2011). As has been recognized as one of the most serious inorganic contaminants in drinking water (Smedley and Kinniburgh, 2002). In areas where groundwater is used as drinking water, high As concentration in groundwater poses a great threat to human health.

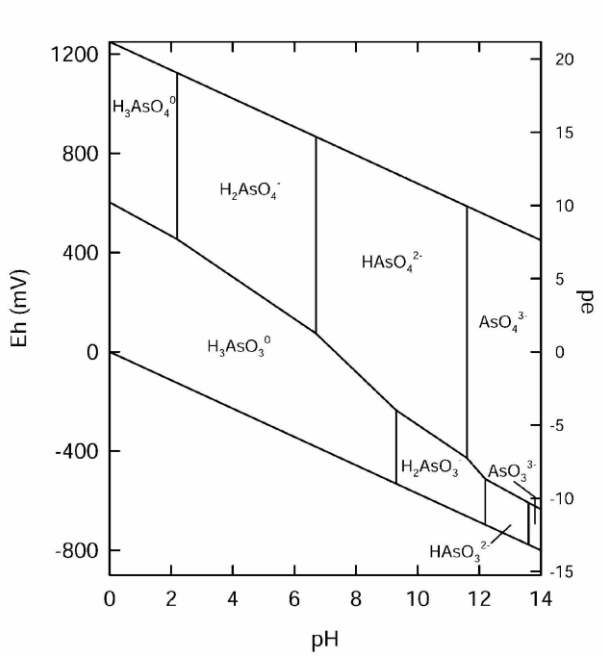

Fig. 1.1: Eh-pH diagram for aqueous As species in the system As–O_2–H_2O at 25 ℃ and 1 bar total pressure (after Smedley and Kinniburgh 2002).

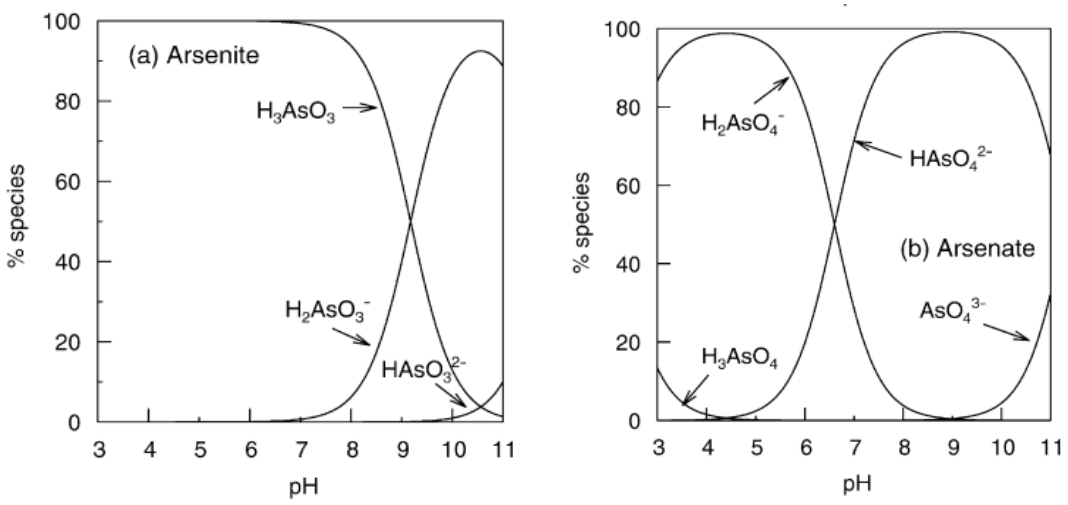

Fig. 1.2: Arsenite (a) and arsenate (b) speciation as a function of pH (ionic strength of about 0.01M) (after Smedley and Kinniburgh 2002).

As concentration in groundwater is controlled by As release from natural minerals (Smedley and Kinniburgh, 2002). As mobilization and transport in groundwater could lead to contamination in adjacent areas (Haque and Johannesson, 2006; Serpa, 2009). Mobility of As in groundwater is influenced by complicated and

coupled processes, which include oxidation and reduction, precipitation and dissolution, and adsorption and desorption. Among these processes, As adsorption to and desorption from subsurface sediments are among the most important reactions that control As movement in aquifers (Yolcubal and Akyol, 2008). Laboratory studies have shown that adsorption can increase As retardation, thereby reduces As transport (Williams, et al., 2003; Yolcubal and Akyol, 2008). Metal oxides are commonly considered to be an important mineral that controls As adsorption and redox reactions (Williams, et al., 2003; Sharma, et al., 2011). Anions such as phosphate and carbonate are shown to compete for sorptive sites on sediment surface and influence As mobility and transport (Darland and Inskeep, 1997; Radu, et al., 2005).

Natural particulate matters such as natural organic matter (NOM) and mineral colloids are important factors influencing As migration in subsurface environment due to their strong affinity to As and the high mobility of themselves (Guo, et al., 2011; Sharma, et al., 2011). Field investigations showed that up to 80%−90% of As were associated with organic and inorganic colloids and slightly larger particles (Baumann, et al., 2006; Guo, et al., 2011). In column leaching experiments using As contaminated sediments, higher As was usually found in leachates with higher turbidity and colloidal particle concentration, indicating As association with mobilized colloids (Ishak, et al., 2002; Ghosh, et al., 2006; Slowey, et al., 2007; Hu, et al., 2008; Tindale, et al., 2011). The presence of NOM was found to increase As mobilization from contaminated sediments (Tessema and Kosmus, 2001; Ko, et al., 2004; Bauer and

Blodau, 2006; Dobran and Zagury, 2006; Sharma and Kappler, 2011). Although the above research suggested As mobilization was related to the mobilization of natural colloids, few studies have been conducted to directly examine the role of natural organic colloids (e.g., NOM) or mineral colloids in As transport (Zhang and Selim, 2007; Sharma, et al., 2011). Natural mineral colloids, NOM, and As often co-exist in subsurface environment, however, even fewer studies have been conducted to investigate the synergic effects of NOM and mineral colloids (Chen, et al., 2008). Investigations are needed to elucidate the influence of NOM and mineral colloids on As transport in groundwater.

1.2 Natural occurrence, speciation, toxicity, and migration of uranium in subsurface environment

Uranium (U) is the heaviest naturally occurring element and is widely distributed in a variety of minerals such as phosphate rock, lignite, and monazite sands (Ribera, et al., 1996). The main natural sources of U are sedimentary rocks, hydrothermal springs, and pyritic conglomerate beds, with an average U concentration of 4 grams/tonne in earth crust (Ribera, et al., 1996). In groundwater, different types of U-bearing rocks are the primary source of uranium (Chau, et al., 2011). Typical concentrations of U in groundwater range from 0.003 to 400 μg/L, however, the concentrations of U can reach the order of 10,000μg/L in waters associated with U mines (Chau, et al., 2011).

U has four oxidation states (+3, +4, +5, and +6), with U(IV) and U(VI) being the most important (Ribera, et al., 1996; Kronfeld, et al., 2004). U(IV) predominates

under reducing conditions for a wide range of pH and is less mobile in aquatic environment compared to U(VI), which is dominant under oxidizing conditions (Kronfeld, et al., 2004; Chau, et al., 2011). U(VI) often occurs as uranyl ion (UO_2^{2+}) and is able to form soluble complexes with carbonate, phosphate, sulfate, fluoride, silicate ions, and many organic ligands in aquatic environment, thus affecting the solubility and mobility of U in groundwater (Ivanovich and Harmon, 1992; Chau, et al., 2011). The forms of aqueous U in weakly mineralized water are controlled by pH and redox potential (Eh) (Fig. 1.3) (Chau, et al., 2011).

U presents radioactive and/or chemical toxicity to human health (Ribera, et al., 1996). Compared to its radioactive toxicity, chemical toxicity of U via ingestion of U contaminated water and food raised more attention (Zamora, et al., 1998; Kurttio, et al., 2002; Kurttio, et al., 2006). Exposure to elevated level of U could lead to nephrotoxic effects and kidney diseases (Zamora, et al., 1998; Kurttio, et al., 2002; Chen, et al., 2004; Kurttio, et al., 2006). The maximum acceptable concentration (MAC) of U in drinking water recommended by Health Canada is 20 μg/L (Health Canada, 2009).

U migration in groundwater is controlled by interactions between U and aquifer materials. Adsorption of U onto aquifer materials is among the most important interactions governing U mobility and transport in subsurface (Gabriel, et al., 1998; Barnett, et al., 2000). Adsorption and transport of U are dependent on several factors including redox potential (Mibus, et al., 2007), pH (Chen and Yiacoumi, 2002),

strength of adsorbents (Ames, et al., 1983; Waite, et al., 1994), presence of complexation ligands/ions (Payne, et al., 1996; Bargar, et al., 1999), and presence of organic or inorganic colloids (Artinger, et al., 2002; Celine, et al., 2009). Solubility of U (IV) is extremely low; therefore reducing conditions effectively immobilize uranium (Duff, et al., 1999). pH controls the species of U in aqueous environment (Waite, et al., 1994), thereby influencing U adsorption and transport. Under oxidizing conditions, U is mainly present as uranyl ions (UO_2^{2+}) at acidic pH and as U-carbonate complexes (e.g., $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) at alkaline pH in systems open to atmosphere (Hsi and Langmuir, 1985; Waite, et al., 1994). U adsorbs to a variety of minerals to different extent (Ames, et al., 1983; Arnold, et al., 1998; Prikryl, et al., 2001a; Li, et al., 2013). Adsorption of U to metal oxides (especially Fe oxides) has been extensively studied due to metal oxides' strong affinity to U (Hsi and Langmuir, 1985; Waite, et al., 1994; Walter, et al., 2003; Shuibo, et al., 2009). The presence of complexation ions such as carbonates effectively decrease U(VI) adsorption to soil particles through the formation of negatively-charged carbonate complexes such as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. These U-carbonate complexes have much lower affinity to solid surface compared to uranyl ions and U hydroxyl complexes, thereby decreasing U adsorption and increasing U transport (Bargar, et al., 1999; Barnett, et al., 2000; Wazne, et al., 2003). Some natural organic and inorganic particulate matters, such as humic substance and mineral colloids, have high affinity to U (Sachs and Bernhard, 2008; Bachmaf and Merkel, 2011; Campos, et al., 2013).

Due to their high mobility in aqueous environment, these organic and inorganic particulate matters may enhance the transport of associated U (Mibus, et al., 2007; Crancon, et al., 2010; Yang, et al., 2012).

In natural environment, NOM, mineral colloids and contaminants usually co-exist and interact in ways that depend on water chemistry (Yang, et al., 2013). Although transport of U in groundwater has attracted extensive research, fewer studies focused on the influence of natural organic compounds and inorganic colloids on U transport (Andersson, et al., 2001; Mibus, et al., 2007; Yang, et al., 2012). Furthermore, previous studies mainly focused on the respective effects of natural organic compounds or inorganic colloids. In order to fully understand U transport in natural subsurface environment, it is necessary to identify the interactions among natural organic compounds, inorganic colloids, and U under ambient environment.

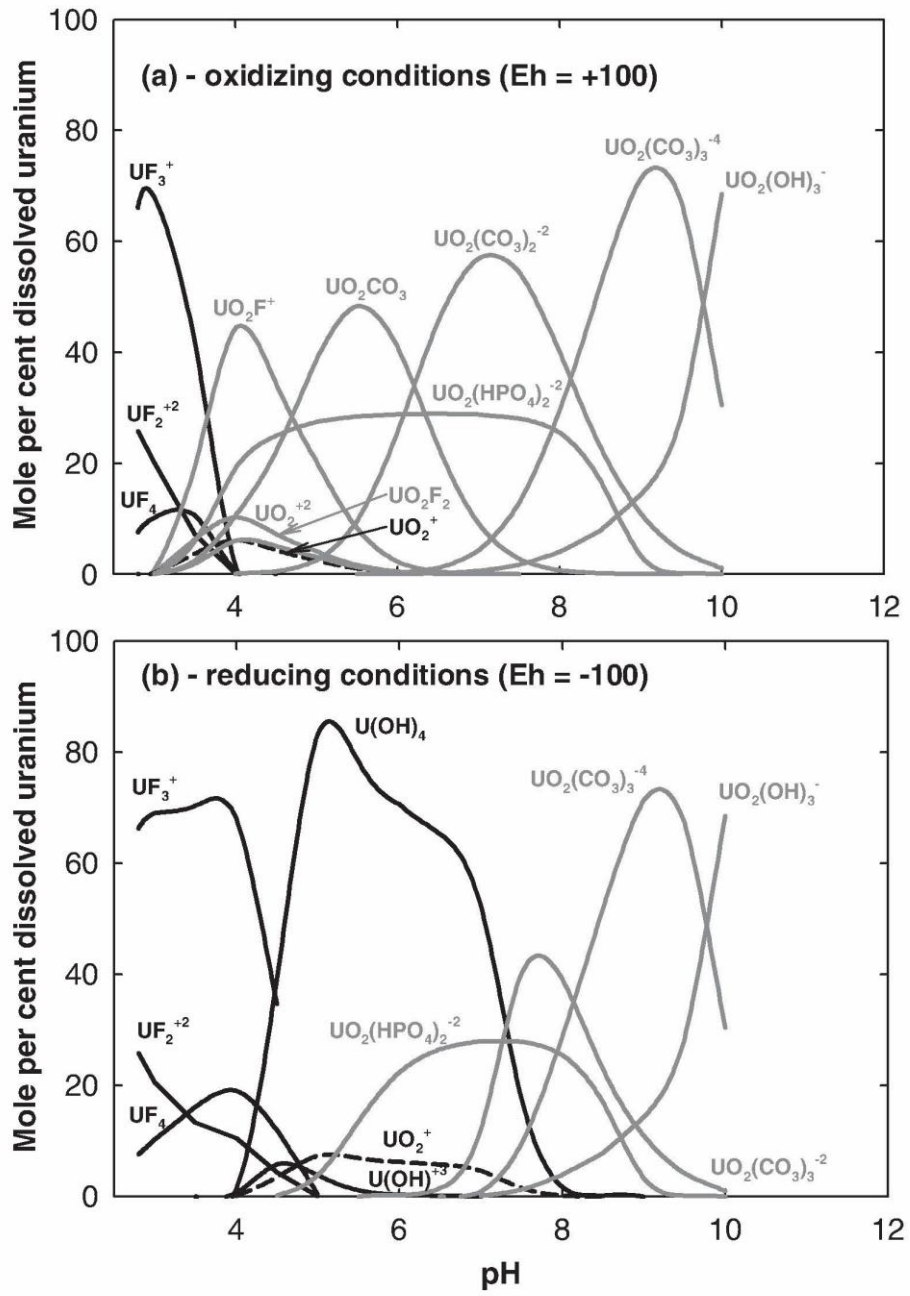

Fig. 1.3: U(VI) (a) and U(IV) speciation in groundwater at 10 ℃ as a function of pH, calculated using PHREEQC-2 code (after Chau, et al., 2011).

1.3 Thesis objectives

The intention of this thesis research is to investigate the influence of natural organic matter (NOM) and mineral colloids on As and U transport in porous media

under ambient water chemistry conditions, with special emphasis on the combined effects of NOM and mineral colloids on As and U transport. The findings of this research are described in the following two chapters.

Chapter 2 investigated the influence of mineral colloids and humic substances on As transport in water-saturated sand columns at pH 5 and pH 9. Illite was used as a representative mineral colloid and humic acid (HA) as humic substance. Our results showed that illite colloids had minor effect on As transport at both pH 5 and pH 9, although illite transport was high at pH 9. HA greatly enhanced As and illite colloid transport at pH 5, but only moderately increased As transport at pH 9. The co-existence of illite and HA at both pH 5 and pH 9 had a weaker ability to facilitate As transport compared to that in HA only systems, indicating that illite colloid hindered the HA-facilitated As transport.

Chapter 3 investigated the influence of natural organic matter and mineral colloids on U transport in porous media. Column transport experiments indicated that HA consistently facilitated U transport under all experimental conditions. However, illite colloids had negligible influent on U transport at pH 5, and decreased U transport at pH 9. Highest U transport was obtained in the presence of both HA and illite colloids at both pH 5 and pH 9.

Overall, the study presented in this thesis demonstrated the importance of NOM and mineral colloids in controlling As and U transport in porous media. This research also showed the influence of water chemistry on the interactions between As or U with

NOM and mineral colloids. Results from this study will improve the prediction of As and U transport and their concentration in groundwater.

1.4 Co-authorship statement

I am the author of this thesis. The manuscripts (Chapter 2 and Chapter 3 of this thesis) were co-authored by my supervisor (Dr. Tao Cheng). I am the principal author for all aspects of this thesis research including the MSc research proposal, experimental design, implementation of the experiments, data collection and analysis, and manuscript preparation. I completed literature review and thesis research proposal under the guidance of my supervisor. The experimental methods described in Chapter 2 and Chapter 3 were designed and decided after thorough discussions with my supervisor. I collected the natural sediment sample with the assistance from Md. Samrat Alam and my supervisor. I characterized the sediment samples with the assistance from Wanda Aylward (XRD) and Lakmali Hewa (sequential extraction). I set up the laboratory experiment systems for column experiments and performed the column experiments. I prepared the samples for ICP-MS analysis with the assistance from Lakmali Hewa. I measured the zeta potential and particle size of the colloid suspension with the assistance from Donna Jackman. I processed all the raw data, and analyzed the data with the guidance from my supervisor.

1.5 References

Abbasnejad, A., Mirzaie, A., Derakhshani, R., and Esmaeilzadeh, E. (2013). Arsenic in groundwaters of the alluvial aquifer of Bardsir plain, SE Iran. *Environmental Earth Sciences, 69*(8), 2549-2557.

Ahmed, K. M., Bhattacharya, P., Hasan, M. A., Akhter, S. H., Alam, S. M. M., Bhuyian, M. A. H., Imam, M. B., Khan, A. A., and Sracek, O. (2004). Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. *Applied Geochemistry, 19*(2), 181-200.

Aiuppa, A., Avino, R., Brusca, L., Caliro, S., Chiodini, G., D'Alessandro, W., Favara, R., Federico, C., Ginevra, W., Inguaggiato, S., Longo, M., Pecoraino, G., and Valenza, M. (2006). Mineral control of arsenic content in thermal waters from volcano-hosted hydrothermal systems: Insights from island of Ischia and Phlegrean Fields (Campanian Volcanic Province, Italy). *Chemical Geology, 229*(4), 313-330.

Akter, A., and Ali, M. H. (2011). Arsenic contamination in groundwater and its proposed remedial measures. *International Journal of Environmental Science and Technology, 8*(2), 433-443.

Ames, L. L., McGarrah, J. E., and Walker, B. A. (1983). Sorption of Uranium and Radium by Biotite, Muscovite, and Phlogopite. *Clays and Clay Minerals, 31*(5), 343-351.

Andersson, P. S., Porcelli, D., Gustafsson, Ö., Ingri, J., and Wasserburg, G. J. (2001).

The importance of colloids for the behavior of uranium isotopes in the low-salinity zone of a stable estuary. *Geochimica Et Cosmochimica Acta, 65*(1), 13-25.

Arnold, T., Zorn, T., Bernhard, G., and Nitsche, H. (1998). Sorption of uranium(VI) onto phyllite. *Chemical Geology, 151*(1–4), 129-141.

Artinger, R., Rabung, T., Kim, J. I., Sachs, S., Schmeide, K., Heise, K. H., Bernhard, G., and Nitsche, H. (2002). Humic colloid-borne migration of uranium in sand columns. *Journal of Contaminant Hydrology, 58*(1–2), 1-12.

Bachmaf, S., and Merkel, B. J. (2011). Sorption of uranium(VI) at the clay mineral-water interface. *Environmental Earth Sciences, 63*(5), 925-934.

Bargar, J. R., Reitmeyer, R., and Davis, J. A. (1999). Spectroscopic confirmation of uranium(VI)-carbonato adsorption complexes on hematite. *Environmental Science & Technology, 33*(14), 2481-2484.

Barnett, M. O., Jardine, P. M., Brooks, S. C., and Selim, H. M. (2000). Adsorption and transport of uranium(VI) in subsurface media. *Soil Science Society of America Journal, 64*(3), 908-917.

Bauer, M., and Blodau, C. (2006). Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. *Science of the Total Environment, 354*(2-3), 179-190.

Baumann, T., Fruhstorfer, P., Klein, T., and Niessner, R. (2006). Colloid and heavy metal transport at landfill sites in direct contact with groundwater. *Water*

Research, 40(14), 2776-2786.

Betcher, R. N., Gascoyne, M., and Brown, D. (1988). Uranium in groundwater of southeastern Manitoba, Canada. *Canadian Journal of Earth Sciences, 25*(12), 2089-2103.

Boyle, D. R., Turner, R. J. W., and Hall, G. E. M. (1998). Anomalous arsenic concentrations in groundwaters of an island community, Bowen Island, British Columbia. *Environmental Geochemistry and Health, 20*(4), 199-212.

Campos, B., Aguilar-Carrillo, J., Algarra, M., Gonçalves, M. A., Rodríguez-Castellón, E., Esteves da Silva, J. C. G., and Bobos, I. (2013). Adsorption of uranyl ions on kaolinite, montmorillonite, humic acid and composite clay material. *Applied Clay Science, 85*(0), 53-63.

Celine, C. L., Lespes, G., Dubascoux, S., Aupiais, J., Pointurier, F., and Potin-Gautier, M. (2009). Colloidal transport of uranium in soil: Size fractionation and characterization by field-flow fractionation-multi-detection. *Journal of Chromatography A, 1216*(52), 9113-9119.

Chau, N. D., Dulinski, M., Jodlowski, P., Nowak, J., Rozanski, K., Sleziak, M., and Wachniew, P. (2011). Natural radioactivity in groundwater - a review. *Isotopes in Environmental and Health Studies, 47*(4), 415-437.

Chen, J., Meyerhof, D. P., and Tracy, B. L. (2004). Model results of kidney burdens from uranium intakes. *Health Physics, 86*(1), 3-11.

Chen, J. P., and Yiacoumi, S. (2002). Modeling of depleted uranium transport in

subsurface systems. *Water Air and Soil Pollution, 140*(1-4), 173-201.

Chen, Z. R., Cai, Y., Liu, G. L., Solo-Gabriele, H., Snyder, G. H., and Cisar, J. L. (2008). Role of soil-derived dissolved substances in arsenic transport and transformation in laboratory experiments. *Science of the Total Environment, 406*(1-2), 180-189.

Cohen, S. M., Arnold, L. L., Eldan, M., Lewis, A. S., and Beck, B. D. (2006). Methylated arsenicals: The implications of metabolism and carcinogenicity studies in rodents to human risk assessment. *Critical Reviews in Toxicology, 36*(2), 99-133.

Crancon, P., Pili, E., and Charlet, L. (2010). Uranium facilitated transport by water-dispersible colloids in field and soil columns. *Science of the Total Environment, 408*(9), 2118-2128.

Darland, J. E., and Inskeep, W. P. (1997). Effects of pH and phosphate competition on the transport of arsenate. *Journal of Environmental Quality, 26*(4), 1133-1139.

Dobran, S., and Zagury, G. J. (2006). Arsenic speciation and mobilization in CCA-contaminated soils: Influence of organic matter content. *Science of the Total Environment, 364*(1-3), 239-250.

Duff, M. C., Hunter, D. B., Bertsch, P. M., and Amrhein, C. (1999). Factors influencing uranium reduction and solubility in evaporation pond sediments. *Biogeochemistry, 45*(1), 95-114.

Gabriel, U., Gaudet, J. P., Spadini, L., and Charlet, L. (1998). Reactive transport of

uranyl in a goethite column: an experimental and modelling study. *Chemical Geology, 151*(1-4), 107-128.

Ghosh, A., Mukiibi, M., S áez, A. E., and Ela, W. P. (2006). Leaching of arsenic from granular ferric hydroxide residuals under mature landfill conditions. *Environmental Science and Technology, 40*(19), 6070-6075.

Grolimund, D., Borkovec, M., Barmettler, K., and Sticher, H. (1996). Colloid-facilitated transport of strongly sorbing contaminants in natural porous media: A laboratory column study. *Environmental Science & Technology, 30*(10), 3118-3123.

Guo, H. M., Zhang, B., Yang, S. Z., Li, Y., Stuben, D., Norra, S., and Wang, J. J. (2009). Role of colloidal particles for hydrogeochemistry in As-affected aquifers of the Hetao Basin, Inner Mongolia. *Geochemical Journal, 43*(4), 227-234.

Guo, H. M., Zhang, B., and Zhang, Y. (2011). Control of organic and iron colloids on arsenic partition and transport in high arsenic groundwaters in the Hetao basin, Inner Mongolia. *Applied Geochemistry, 26*(3), 360-370.

Haque, S., and Johannesson, K. H. (2006). Arsenic concentrations and speciation along a groundwater flow path: The Carrizo Sand aquifer, Texas, USA. *Chemical Geology, 228*(1–3), 57-71.

Health Canada. (2006). Guidelines for Canadian Drinking Water Quality: Guideline Technical Document - Arsenic.

Health Canada. (2009). Guidelines for Canadian Drinking Water Quality: Guideline Technical Document - Radiological Parameters.

Hsi, C. K. D., and Langmuir, D. (1985). Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochimica Et Cosmochimica Acta*, *49*(9), 1931-1941.

Hu, S. P., Chen, X. C., Shi, J. Y., Chen, Y. X., and Lin, Q. (2008). Particle-facilitated lead and arsenic transport in abandoned mine sites soil influenced by simulated acid rain. *Chemosphere*, *71*(11), 2091-2097.

Ishak, C. F., Seaman, J. C., Miller, W. P., and Sumner, M. (2002). Contaminant mobility in soils amended with fly ash and flue-gas gypsum: Intact soil cores and repacked columns. *Water, Air, and Soil Pollution, 134*(1-4), 287-305.

Ivanovich, M., and Harmon, R. S. (1992). *Uranium-series disequilibrium: Applications to earth, marine, and environmental sciences*: Oxford University Press.

Jomova, K., Jenisova, Z., Feszterova, M., Baros, S., Liska, J., Hudecova, D., Rhodes, C. J., and Valko, M. (2011). Arsenic: toxicity, oxidative stress and human disease. *Journal of Applied Toxicology, 31*(2), 95-107.

Ko, I., Kim, J.-Y., and Kim, K.-W. (2004). Arsenic speciation and sorption kinetics in the As–hematite–humic acid system. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 234*(1–3), 43-50.

Kronfeld, J., Godfrey-Smith, D. I., Johannessen, D., and Zentilli, M. (2004). Uranium

series isotopes in the Avon Valley, Nova Scotia. *Journal of Environmental Radioactivity, 73*(3), 335-352.

Kurttio, P., Auvinen, A., Salonen, L., Saha, H., Pekkanen, J., Makelainen, I., Vaisanen, S. B., Penttila, I. M., and Komulainen, H. (2002). Renal effects of uranium in drinking water. *Environmental Health Perspectives, 110*(4), 337-342.

Kurttio, P., Harmoinen, A., Saha, H., Salonen, L., Karpas, Z., Komulainen, H., and Auvinen, A. (2006). Kidney toxicity of ingested uranium from drinking water. *American Journal of Kidney Diseases, 47*(6), 972-982.

Li, X., Wu, J., Liao, J., Zhang, D., Yang, J., Feng, Y., Zeng, J., Wen, W., Yang, Y., Tang, J., and Liu, N. (2013). Adsorption and desorption of uranium (VI) in aerated zone soil. *Journal of Environmental Radioactivity, 115*(0), 143-150.

Maity, J. P., Nath, B., Chen, C. Y., Bhattacharya, P., Sracek, O., Bundschuh, J., Kar, S., Thunvik, R., Chatterjee, D., Ahmed, K. M., Jacks, G., Mukherjee, A. B., and Jean, J. S. (2011). Arsenic-enriched groundwaters of India, Bangladesh and Taiwan-Comparison of hydrochemical characteristics and mobility constraints. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering, 46*(11), 1163-1176.

Mandal, B. K., and Suzuki, K. T. (2002). Arsenic round the world: a review. *Talanta, 58*(1), 201-235.

Mibus, J., Sachs, S., Pfingsten, W., Nebelung, C., and Bernhard, G. (2007). Migration of uranium(IV)/(VI) in the presence of humic acids in quartz sand: A

laboratory column study. *Journal of Contaminant Hydrology, 89*(3-4), 199-217.

Patel, K. S., Shrivas, K., Brandt, R., Jakubowski, N., Corns, W., and Hoffmann, P. (2005). Arsenic contamination in water, soil, sediment and rice of central India. *Environmental Geochemistry and Health, 27*(2), 131-145.

Payne, T. E., Davis, J. A., and Waite, T. D. (1996). Uranium adsorption on ferrihydrite - Effects of phosphate and humic acid. *Radiochimica Acta, 74*, 239-243.

Prikryl, J. D., Jain, A., Turner, D. R., and Pabalan, R. T. (2001). Uranium(VI) sorption behavior on silicate mineral mixtures. *Journal of Contaminant Hydrology, 47*(2-4), 241-253.

Radu, T., Subacz, J. L., Phillippi, J. M., and Barnett, M. O. (2005). Effects of dissolved carbonate on arsenic adsorption and mobility. *Environmental Science & Technology, 39*(20), 7875-7882.

Ribera, D., Labrot, F., Tisnerat, G., and Narbonne, J. F. (1996). Uranium in the environment: occurrence, transfer, and biological effects. *Reviews of environmental contamination and toxicology, 146*, 53.

Sachs, S., and Bernhard, G. (2008). Sorption of U(VI) onto an artificial humic substance-kaolinite-associate. *Chemosphere, 72*(10), 1441-1447.

Schmitt, D., Saravia, F., Frimmel, F. H., and Schuessler, W. (2003). NOM-facilitated transport of metal ions in aquifers: importance of complex-dissociation kinetics and colloid formation. *Water Research, 37*(15), 3541-3550.

Serpa, C., Batterson, M. and Guzzwell, K. . (2009). The influence of bedrock and mineral occurrences on Arsenic concentrations in groundwater wells in the Gander Bay Area, Newfoundland. *Current Research (2009) Newfoundland and Labrador Department of Natural Resources Geological Survey*(Report 09-1), 315-337.

Sharma, P., and Kappler, A. (2011). Desorption of arsenic from clay and humic acid-coated clay by dissolved phosphate and silicate. *Journal of Contaminant Hydrology, 126*(3-4), 216-225.

Sharma, P., Rolle, M., Kocar, B., Fendorf, S., and Kappler, A. (2011). Influence of Natural Organic Matter on As Transport and Retention. *Environmental Science & Technology, 45*(2), 546-553.

Shuibo, X., Chun, Z., Xinghuo, Z., Jing, Y., Xiaojian, Z., and Jingsong, W. (2009). Removal of uranium (VI) from aqueous solution by adsorption of hematite. *Journal of Environmental Radioactivity, 100*(2), 162-166.

Slowey, A. J., Johnson, S. B., Newville, M., and Brown Jr, G. E. (2007). Speciation and colloid transport of arsenic from mine tailings. *Applied Geochemistry, 22*(9), 1884-1898.

Smedley, P. L., and Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry, 17*(5), 517-568.

Tatalovich, M. E., Lee, K. Y., and Chrysikopoulos, C. V. (2000). Modeling the

transport of contaminants originating from the dissolution of DNAPL pools in aquifers in the presence of dissolved humic substances. *Transport in Porous Media, 38*(1-2), 93-115.

Tessema, D. A., and Kosmus, W. (2001). Influence of humic and low molecular weight polycarboxylic acids on the release of arsenic from soils. *Journal of Trace and Microprobe Techniques, 19*(2), 267-278.

Tindale, K., Patel, P., and Wallschlager, D. (2011). Colloidal arsenic composition from abandoned gold mine tailing leachates in Nova Scotia, Canada. *Applied Geochemistry, 26*, S260-S262.

Tufano, K. J., and Fendorf, S. (2008). Confounding impacts of iron reduction on arsenic retention. *Environmental Science & Technology, 42*(13), 4777-4783.

Waite, T. D., Davis, J. A., Payne, T. E., Waychunas, G. A., and Xu, N. (1994). Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. *Geochimica Et Cosmochimica Acta, 58*(24), 5465-5478.

Walter, M., Arnold, T., Reich, T., and Bernhard, G. (2003). Sorption of Uranium(VI) onto Ferric Oxides in Sulfate-Rich Acid Waters. *Environmental Science & Technology, 37*(13), 2898-2904.

Wang, S., and Mulligan, C. N. (2006). Occurrence of arsenic contamination in Canada: Sources, behavior and distribution. *Science of the Total Environment, 366*(2-3), 701-721.

Wazne, M., Korfiatis, G. P., and Meng, X. (2003). Carbonate Effects on Hexavalent

Uranium Adsorption by Iron Oxyhydroxide. *Environmental Science & Technology, 37*(16), 3619-3624.

Williams, L. E., Barnett, M. O., Kramer, T. A., and Melville, J. G. (2003). Adsorption and transport of arsenic(V) in experimental subsurface systems. *Journal of Environmental Quality, 32*(3), 841-850.

Yang, Y., Saiers, J. E., and Barnett, M. O. (2013). Impact of Interactions between Natural Organic Matter and Metal Oxides on the Desorption Kinetics of Uranium from Heterogeneous Colloidal Suspensions. *Environmental Science & Technology, 47*(6), 2661-2669.

Yang, Y., Saiers, J. E., Xu, N., Minasian, S. G., Tyliszczak, T., Kozimor, S. A., Shuh, D. K., and Barnett, M. O. (2012). Impact of Natural Organic Matter on Uranium Transport through Saturated Geologic Materials: From Molecular to Column Scale. *Environmental Science & Technology, 46*(11), 5931-5938.

Yolcubal, I., and Akyol, N. H. (2008). Adsorption and transport of arsenate in carbonate-rich soils: Coupled effects of nonlinear and rate-limited sorption. *Chemosphere, 73*(8), 1300-1307.

Zamora, M. L., Tracy, B. L., Zielinski, J. M., Meyerhof, D. P., and Moss, M. A. (1998). Chronic ingestion of uranium in drinking water: A study of kidney bioeffects in humans. *Toxicological Sciences, 43*(1), 68-77.

Zhang, H., and Selim, H. M. (2007). Colloid mobilization and arsenite transport in soil columns: Effect of ionic strength. *Journal of Environmental Quality, 36*(5),

1273-1280.

Chapter 2. Influence of Mineral Colloids and Humic Substances on Arsenate Transport in Water-Saturated Sand Columns

Abstract

The adsorption of contaminants to sub-micrometer sized natural soil components such as mineral colloids and humic substances is an important geochemical process that controls contaminant migration in soil and groundwater. Most previous laboratory studies measured As transport through porous media in the absence of mineral colloids and humic substances. This implies the mobility of As in natural subsurface environments could be very different from that estimated using laboratory experiments. The objective of this study is to examine the influence of illite colloids and humic acid (HA) (representing natural sub-micrometer sized soil components) on As transport. As transport was investigated by injecting As-spiked solution/suspension into water-saturated columns packed with natural sediments and quartz sand, and analyzing As concentration in column effluent. Our results showed that HA substantially increased As transport via (i) competition with As for adsorptive sites on column materials and (ii) formation of aqueous As-HA complexes. The influence of illite colloids on As trasnport was less pronounced due to weak binding between As and illite and/or low illite mobility. When both illite colloids and HA were present, As transport was normally higher than that in HA-free systems, due to HA-enhanced As transport. However, As transport was lower in systems with both illite colloids and HA compared to that in systems with HA but no illite, due to HA adsorption to illite

colloids, which decreased aqueous HA concentration and the magnitude of HA-enhanced As transport. This study demonstrates that both mineral colloids and HA influence As transport but through different mechanisms and leading to different results, and that the combined effects of mineral colloids and HA must be considered when assessing As transport in natural subsurface environments.

Key Words: As transport, colloids, illite, humic acid, adsorption, column experiments

2.1 Introduction

Arsenic (As) is a common groundwater contaminant that poses serious threat to human health (Smedley and Kinniburgh, 2002). Both anthropogenic pollution and natural geochemical processes such as dissolution of As bearing minerals and As desorption from hosting minerals can cause arsenic contamination in groundwater (Boyle, et al., 1998; Smedley and Kinniburgh, 2002; Wang and Mulligan, 2006). Once released to groundwater, As could travel along with groundwater flow and cause contamination in adjacent areas (Haque and Johannesson, 2006; Serpa, 2009). In order to predict the scope of As contamination in groundwater, it is important to understand how As migrates in porous media.

Humic substances (HS) and mineral colloids are ubiquitous in groundwater and the vadose zone. Due to the very large surface area and abundance of surface functional groups, HS and mineral colloids strongly adsorb many aqueous contaminants. Mineral colloids and HS are highly mobile in subsurface environment, therefore the mobility of strongly sorbing contaminants can be substantially increased when these contaminants are associated with colloids or HS. The magnitude of facilitated transport is influenced by the mobility of colloids and HS, as well as the ability of the colloids and HS to retain contaminants. Although colloid- and HS-facilitated transport of heavy metals, radionuclides, and organic contaminants in subsurface environment have been extensively studied (Grolimund, et al., 1996; Tatalovich, et al., 2000; Schmitt, et al., 2003; Yang, et al., 2012), previous and current

research on As transport has focused on transport behaviors of dissolved As in the absence of colloids and HS (Darland and Inskeep, 1997; Williams, et al., 2003; Hossain and Islam, 2008; Hu, et al., 2010). Under natural conditions, however, As in soil and groundwater are found to be associated with mineral colloids and natural organic matter (Paktunc, et al., 2003; Baumann, et al., 2006; Cheng, et al., 2009; Guo, et al., 2009; Guo, et al., 2011). It has been reported that As mobilization occurs concomitantly with the mobilization of inorganic and organic soil particulate matters (Puls and Powell, 1992; Zhang and Selim, 2007; Chen, et al., 2008; Tindale, et al., 2011). Therefore, colloid and HS-facilitated transport of As could be a major mechanism for As transport in groundwater. In order to quantify the As migration in subsurface environment, the role of mineral colloids and HS on As transport needs to be clarified.

In natural subsurface environment, HS, mineral colloids, and contaminants often co-exist. However, most studies on colloid- and HS-facilitated transport focus on the effect of either mineral colloids or HS, but not both. Very limited studies investigated the synergic effects of mineral colloids and HS (Saiers, 2002; Tang and Weisbrod, 2009). HS can form aqueous complexes with contaminants (Datta, et al., 2001; Schmitt, et al., 2003; Metreveli, et al., 2010; Kostic, et al., 2011) and compete with contaminants for surface sites on aquifer materials (Antelo, et al., 2007; Giasuddin, et al., 2007; Wang, et al., 2013). In addition, HS could influence contaminant transport by enhancing the mobility of mineral colloids (Akbour, et al., 2002; Wang and

Mulligan, 2009b) and changing the ability of mineral colloids to retain contaminants (Fairhurst, et al., 1995; Cornu, et al., 1999). The interactions between mineral colloids, HS, and contaminants make quantifying the transport of contaminants in natural subsurface setting a formidable task.

The objective of this paper is to investigate the respective influence of mineral colloids and HS on As transport, as well as the combined effects of mineral colloids and HS. Illite was used as a representative mineral colloid due to its abundance in natural subsurface environment (Gradusov, 1974; Ransom and Helgeson, 1993) and its ability to retain many water-borne contaminants (Polubesova and Nir, 1999; Gu and Evans, 2007; Zhang, et al., 2013). As transport was investigated by injecting As-containing solution or suspension into water-saturated columns packed with natural sediment and quartz sand, and analyzing As concentration in column effluent. Eight column experiments, distinguished based on the composition of the As-containing solution (As only, As + illite, As + HA, and As + illite + HA) and solution pH (pH 5 and pH 9), were performed in order to elucidate the influence of mineral colloids and HS on As transport.

2.2 Materials and Methods

2.2.1 Porous media

The porous media used to pack the columns consists of 4 parts of pure quartz sand and 1 part of natural sediment. The quartz sand (Anachemia, catalog #

71008-394) purchased from VWR is mineralogically pure and contains >99.7 % SiO_2, <0.02% Fe_2O_3, and <0.05% Al_2O_3. The quartz sand was washed with nano-pure water, dried, and sieved to a grain size range of 0.25 to 0.60 mm. The natural sediment was collected from Avondale, a town located in Avalon Peninsula in Eastern Newfoundland. The sediment was air dried and gently ground to smaller fractions to pass a serial of sieves. The sieved fraction with a grain size range between 0.25 and 0.60 mm was collected and stored. Mineral composition of the sieved sediment was determined using X-ray diffraction (XRD), and concentrations of Fe oxides and Al (hydro)oxides in the sieved sediment were determined using a sequential extraction method (Tessier, et al., 1979) and ICP-MS (inductively coupled plasma mass spectrometry) analysis. The above pre-treated quartz sand and natural sediments were combined at a ratio of 4:1 (quartz sand mass to sediment mass), well mixed, and used to pack our columns.

2.2.2 Preparation of solutions and influent colloid suspensions

Unless stated otherwise, all chemicals used were certified ACS grade, and nano-pure water was used for preparation of all solutions and colloid suspensions. As(V) stock solutions (75 mg/L) was prepared by dissolving appropriate amounts of sodium hydrogen arsenate heptahydrate (Alfa Aesar, catalog # 33373-14) in nano-pure water. A commercial humic acid (HA) (Alfa Aesar, catalog # 41747-14) purchased from VWR was used to control HA concentration in influent solutions and suspensions. Colloid stock suspension was prepared with illite (IMt-2, The Clay

Mineral Society) following the method of Saiers and Hornberger (1999). As provided by the supplier, the major chemical composition (mass %) of illite was shown as following: SiO_2: 49.3, Al_2O_3: 24.25, TiO_2: 0.55, Fe_2O_3: 7.32, FeO: 0.55, MnO: 0.03, MgO: 2.56, CaO: 0.43. Four grams (4.0 g) of illite powder was suspended in 1000 mL nano-pure water in a high-density polyethylene bottle. The suspension was vigorously shaken and ultrasonically dispersed for 30 mins. After the ultrasonic bath, the suspension was transferred to an erlenmeyer flask and let stand for 24 hours before the supernatant was transferred to a clean high-density polyethylene bottle. The concentration of illite in the supernatant was measured gravimetrically by filtering 100 mL of the suspension through a 0.1 μm polyethersulfone membrane filter (Pall Life Sciences). The filter was dried in an oven at 60 ℃ before and after the filtration, and the difference between the weights of the filter was considered as the mass of illite colloids. The illite stock suspension was well mixed and diluted to a desired concentration of 100 mg/L 24 hours before used in column experiments.

Four types of As-spiked solutions/suspensions: As only, As + illite, As + HA, and As + illite + HA, were prepared by directly adding HA and diluting stock solution of As and illite stock suspension (Table 2.1). The ionic strength was adjusted to 0.01 M using NaCl. Concentration of As, HA, and illite colloids in these As-spiked solutions/suspensions were 750 μg/L, 12 mg (organic carbon)/L, and 100 mg/L. As-free background solution was prepared for use in column experiments to pack and precondition the columns. The background solutions had the same ionic strength (0.01

M NaCl) as the As-spiked solution/suspension, and contained 12 mg (organic carbon)/L HA (for As + HA and As + illite + HA experiments), or was HA-free (for As only and As + illite experiments). All the As-spiked solutions/suspensions and the background solutions were adjusted to desired pH (5 or 9) using HCl and NaOH before used in column experiments.

2.2.3 Characterization of influent illite colloid suspensions

Zeta potential and particle size of illite colloids in the influent illite suspensions were determined using a Zetasizer Nano-ZS (Malvern) following dilution of the suspension samples with water of the same pH, electrolyte and humic acid composition as used in the column experiment. To quantity As adsorbed to illite colloids in the influent suspensions, well-mixed illite suspensions were filtered through 0.1 μm polyethersulfone membrane filters (Pall Life Sciences), and As concentration in the suspension and the filtrate was analyzed (following the methods described in 2.2.5). The difference between As concentration in the suspension and the filtrate was considered as As adsorbed to illite colloids.

2.2.4 Column experiments

Column experiments were conducted using a Kontes ChromaFlex™ Chromatography Column (2.5 cm inner diameter, 15 cm length). Eight column experiments, distinguished by solution pH and composition of the As-spiked solution/suspension, were conducted (Table 2.1). Each of the eight experiments was

conducted in duplicate. For each column experiment, a vertically oriented column was wet-packed by slowly pouring well-mixed porous media (described in 2.2.1) into the column, with simultaneous tapping to make it uniformly packed and to remove any trapped air bubbles. Dry mass of the porous media and volume of the solution used to pack the column was recorded. The average dry mass of the porous media and average volume of background solution used to pack the column (i.e., pore volume) was 127 g and 23 cm^3 respectively, corresponding to a bulk density of 1.73 g/cm^3 and a porosity of 0.31. Immediately after packing, a peristaltic pump (Masterflex, Cole-Parmer Instruments) was used to inject background solution to the column base at a specific discharge of 0.66 cm/min until the pH of the effluent (from the top of the column) became stable. This precondition step normally took 18 hours to complete. After precondition, column influent was switched from the background solution to As-spiked solution/suspension (refer to Table 2.1). Ten pore volumes (10 Vp) of the As-spiked influent were injected into the column. The specific discharge in all the column experiments was maintained at 0.66 cm/min. Effluent samples (from the top of the column) were collected with a fraction collector (CF-2, Spectrum Chromatography) for analyses of As and illite concentrations.

2.2.5 Analytical methods

For As and illite concentration determination, 1.0000 g of well mixed influent or effluent sample was transferred to a Teflon screw cap jar, mixed with 1 mL 16 mol/L HNO_3 and kept on a hot plate at 70 ℃ for 24 hours. Then the solution was transferred

to a clean tube and diluted to 20.00 g before sent for ICP-MS analysis of As and Fe concentrations. Our tests showed this method was able to recover more than 101.4 ± 6.9 % of As even when high concentrations of illite (100 mg/L) were present. Illite concentrations in the effluent samples were calculated based on ICP-MS measured Fe concentration of the sample and a calibration curve made with a series of samples containing known concentrations of illite colloids and measured Fe concentrations (Grolimund, et al., 1996).

2.3 Results and Discussion

2.3.1 Mineral and elemental composition of till sediment

X-ray diffraction (XRD) indicated albite (50.5% mass), quartz (34.9% mass) and muscovite (14.7% mass) were the major minerals in the sieved till sample. Metal (Fe and Al) oxides were not detected by XRD, indicating their concnetrations were below the detection limit of XRD (~5% total mass). Sequential extraction and elemental analysis showed the concentration of Fe and Al oxides were 3592 mg (as Fe) /kg and 1057 mg (as Al) /kg respectively.

2.3.2 Characterizations of influent illite colloid suspensions, and As adsorption to illite

In the absence of HA, illite colloids were negatively charged at both pH 5 and 9 (Table 2.1), consistent with the point of zero charge of illite (pH_{pzc} = 2.5) (Kosmulski, 2011). In the presence of HA, illite colloids became slightly more negatively charged

at both pH, indicating adsorption of negatively charged HA (pK_1=3.7 ± 0.1, pK_2=6.6 ± 0.1, (Tombacz, et al., 2000) to illite. HA adsorbs to clay minerals through association with poly-valent metals (e.g., Al(III)) on clay surface (Greenland, 1971), van der Waals interactions, bridging by aqueous poly-valent metal cations (e.g., Ca^{2+}, Pb^{2+}), and ion/ligand exchange (Liu and Gonzalez, 1999; Arnarson and Keil, 2000).

Table 2.1: Conditions of column experiments and properties of illite colloids.

pH	As Influent	Zeta Potential (mV)	Particle Size (d. nm)	% As attached to illite
5	As	NA	NA	NA
	As + illite	-42.9 ± 0.1	248.8 ± 7.6	8.5 ± 3.7 %
	As + HA	NA	NA	NA
	As + illite + HA	-43.8 ± 1.5	262.2 ± 1.0	5.0 ± 3.8 %
9	As	NA	NA	NA
	As + illite	-36.5 ± 4.4	276.2 ± 14.0	4.7 ± 3.8 %
	As + HA	NA	NA	NA
	As + illite +HA	-40.6 ± 0.4	259.8 ± 20.8	-3.4 ± 4.1 %

At pH 5, the size of illite colloids seemed slightly higher in the presence of HA (262.2 ± 1.0 nm vs. 248.8 ± 7.6 nm, Table 2.1); while at pH 9, the measured size of illite seemed slightly lower in the presence of HA (259.8 ± 20.8 nm vs. 276.2 ± 14.0 nm, Table 2.1). However, t-test revealed that the difference was insignificant at both pH 5 and 9 ($p > 0.05$), indicating HA adsorption to illite did not significantly change the size of illite colloids. The measured average diameter of illite colloids was in the range of 244~276 nm (Table 2.1), much larger than the pore size of the membrane filters used in our filtration (100 nm), therefore the filtration process was expected to

retain most of the illite colloids, and As in the filtrate represents aqueous phase As (i.e., As not associated with illite).

In the absence of HA, 8.5 ± 3.7 % of As in the influent was attached to illite at pH 5 and 4.7 ± 3.8 % of As was attached to illite at pH 9 (Table 2.1), indicating As adsorption to illite decreased with increasing pH. As adsorption to clay minerals could be ascribed to surface complexation with octahedrally coordinate aluminium (Halter and Pfeifer, 2001) and adsorption to electropositive hydroxides coatings (e.g., Fe, Al and Ca (oxy)hydroxides) on clay (Goldberg, 2002). At low pH, protonatation of hydroxyl groups on clay mineral could provide extra adsorption sites to As anions (Mohapatra, et al., 2007). In the presence of HA, As adsorption decreased from 8.5 ± 3.7 % to 5.0 ± 3.8 % at pH 5 and from 4.7 ± 3.8 % to -3.4 ± 4.1 % at pH 9 (Table 2.1). This decrease was attributed to competitive adsorption between HA and As, since HA and As are both negatively charged and adsorb to illite via similar mechanisms (e.g., surface complexation with Al(III) on clay surface).

2.3.3 Illite transport

Illite trasnport was strongly influenced by solution pH and HA. At pH 5, illite transport was very low in the absence of HA: the overall illite recovery in the effluent was practically zero, indicating all the injected illite deposited in the column (Table 2.2). In contrast, illite trasnport was much higher at pH 5 in the presence of HA, in the As + illite + HA experiment effluent illite concentration reached 0.72 ± 0.08 at 4 Vp (pore volume) and 1.00 ± 0.06 at 10 Vp (Fig. 2.1a), and the overall illite recovery in

the effluent was 62.6 ± 1.9 % (Table 2.2). At pH 9, illite transport was high for both the As + illite and the As + illite + HA experiments (Fig. 2.1b): complete illite breakthrough (i.e., $C/C_0 = 1$) occurred at 2 Vp and illite breakthrough was similar to that of a conservative tracer. At pH 9, illite transport was slightly higher in the presence of HA, and in some effluent samples colloid concentration was slightly higher than 1 (Fig. 2.1b). The overall illite recovery in the effluent was 93.3 ± 1.0 % in As + illite experiment and 103.6 ± 2.8 % in As + illite + HA experiment (Table 2.2). The >100% illite recovery in the presence of HA at pH 9 was presumably due to elution of small particles that were originally contained in the till sediment.

Table 2.2: As and illite colloids recovery in column experiments.

pH	Influent	% As Recovery	% Colloid Recovery
5	As	0	NA
	As + illite	0	0
	As + HA	21.3 ± 2.8 %	NA
	As + illite + HA	11.3 ± 0.5 %	62.6 ± 1.9 %
9	As	53.3 ± 8.6 %	NA
	As + illite	44.6 ± 3.4 %	93.3 ± 1.0 %
	As + HA	62.1 ± 6.0 %	NA
	As + illite +HA	55.4 ± 1.1 %	103.6 ± 2.8 %

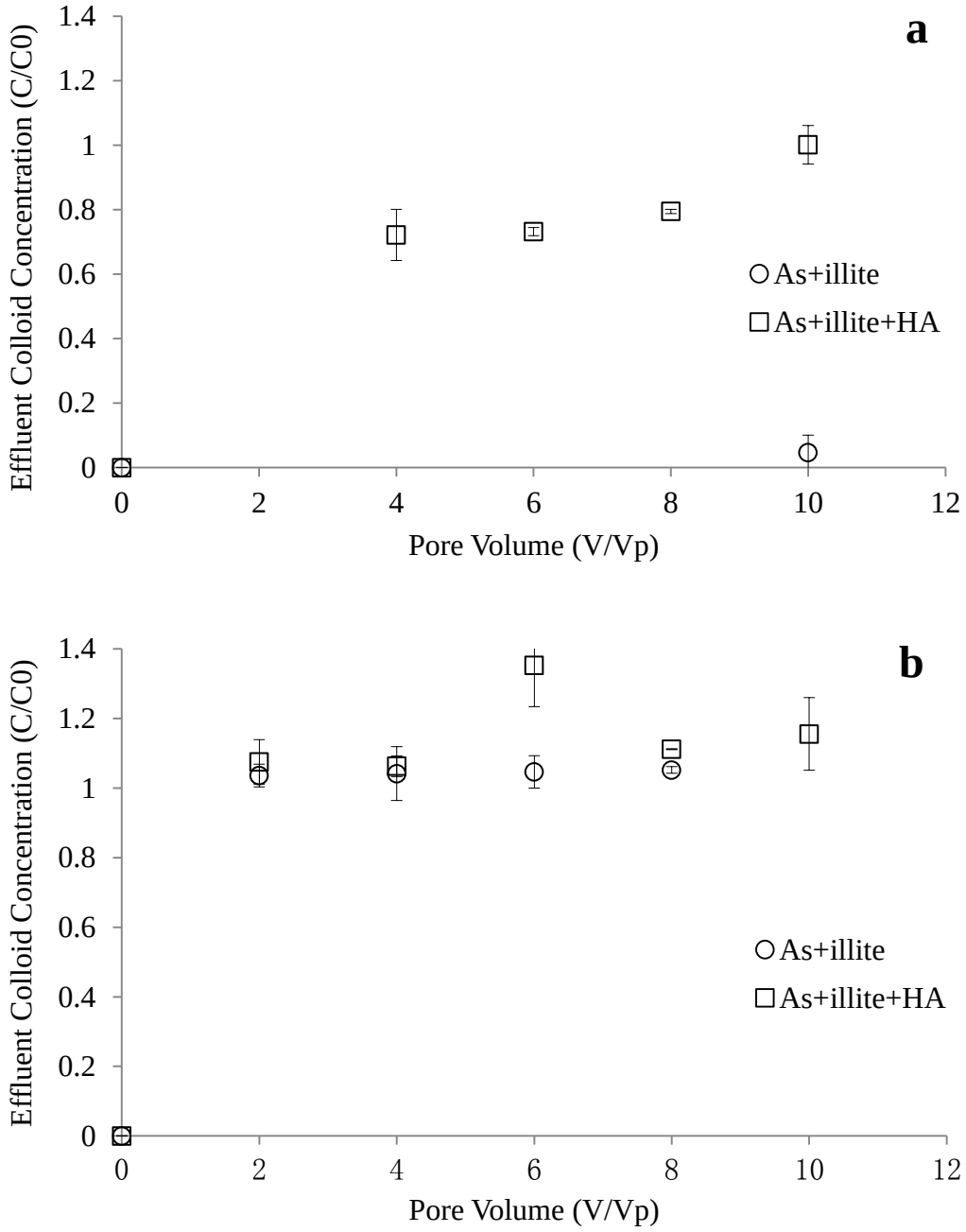

Fig. 2.1: Breakthrough curves of colloidal particles through columns filled with the mixture of till and quartz sand in the absence and presence of humic acid (HA) at pH 5 (a) and pH 9 (b).

Transport of colloids in porous media is influenced by colloid deposition onto sand, and the deposition rate depends on the overall effect of the interactive forces (van der Waals forces, electric double layer interactions, hydration forces, and steric

repulsion) between colloid and collector (Kretzschmar, et al., 1999). A higher deposition rate results in lower transport. In our column experiemnts, dominant minerals such as albite, quartz, and muscovite could all interact with illite and contribute to illite deposition. However, in the pH range of our experiemnts, deposition of illite to these silicate minerals is expected to be low since both illite and the minerals are negatively charged (pH_{pzc} of quartz < 3, albite < 2, muscovite < 4) (Kosmulski, 2011), and depostion is under unfavorable conditions. The low transport of illite at pH 5 in the absence of HA was attributed to illite deposition onto metal (e.g., Fe and Al) oxides. As indicated by our extraction experiments, Fe and Al oxides were present in our column filling at concentration of 718 mg (as Fe) / kg column filling and 211 mg (as Al) / kg column filling. Although metal oxides are usually minor components in natural sediments, they substantially influence colloid depostion and transport (Johnson, et al., 1996; McCarthy and McKay, 2004; Zhang, et al., 2010). The strong influence of metal oxides on colloid depostion is due to the high point of zero charge (pH_{zpc}) of metal oxides. Reported pH_{zpc} ranges from 7.8 to 8.5 for Fe oxides (Darland and Inskeep, 1997) and from 6.5 to 7 for Al oxides (Xu, et al., 1991). Under ambient groundwater pH, Fe and Al oxides could carry positive charges, and therefore strongly attract negatively charged collids through electric double layer forces. Fe oxides can be the most important mineral that controls colloid depostion (Johnson, et al., 1996; McCarthy and McKay, 2004; Zhang, et al., 2010). Based on the pH_{zpc} of Fe and Al oxides, in our As + illite experiments, Fe and Al oxides carried positive charges

at pH 5 due to protonation of surface sites. While at pH 9, these metal oxides carried negative charges due to deprotonation. According to the zeta potential of our colloidal suspensions, illite colloids were negatively charged at both pH 5 and 9 (Table 2.1). Therefore, nearly complete colloid deposition occurred at pH 5 due to the strong electrostatic attractions between negatively charged illite colloids and positive metal oxides. At pH 9, repulsion between the negatively charged illite colloids and metal oxides led to complete illite breakthrough.

The higher transport of illite in the presence of HA was attributed to HA adsorption to column materials (especially Fe and Al oxides) and illite colloids. Enhanced mobility of colloidal particles by natural organic matter was observed previously by other researchers (Laegdsmand, et al., 2005; Wang and Mulligan, 2009b). Natural organic matter such as HA adsorbs to many minerals including clays (discussed in 2.3.2) and metal oxides (Cornu, et al., 1999; Liu and Gonzalez, 1999; Akbour, et al., 2002; Redman, et al., 2002). HA adsorbs to metal oxides by electrostatic interactions, association via aliphatic/aromatic carbon, and ligand exchange or H-bonding with carboxyl/ hydroxyl functional groups (Tipping, 1981; Gu, et al., 1994; Fein, et al., 1999; Borggaard, et al., 2005; Yang, et al., 2013). In the pH range (5−9) used in our experiments, HA carries negative charges due to the dissociation of the acidic groups ($pK_1 = 3.7 \pm 0.1$, $pK_2 = 6.6 \pm 0.1$) (Kretzschmar, et al., 1999; Tombacz, et al., 2000). At pH 5, negatively charged HA strongly adsorbed to positively charged metal (Fe and Al) oxides, which diminished or even reversed the

positive charges on metal oxides and therefore hindered the deposition of negatively charged illite colloids, leading to increased illite transport. At pH 9, metal oxides were negatively charged, and adsorption of negatively charged HA to metal oxides was weak. Therefore only slight increase in illite transport was observed at pH 9.

Besides adsorption to column materials, negatively charged HA also adsorbs to illite colloids (discussed in 2.3.2), which increased the negative charges on illite (Table 2.1) and contributed to the increased colloid transport due to electrostatic repulsive interaction between HA-coated colloids and column materials (Chen, et al., 2012). Steric repulsive forces between HA-coated colloids and column materials may also increase the mobility of illite colloids (Kretzschmar, et al., 1999; Chen, et al., 2012).

2.3.4 As transport

As breakthrough curves in column experiments through the mixture of natural sediment and quartz sand in the absence and presence of humic acid (HA) and illite colloids at pH 5 and 9 were obtained by plotting the relative concentration of As in effluent samples (C/C_0, C: As concentration in the effluent samples; C_0: As concentration in the influent solution/suspension) to the pore volumes (V/Vp, V: Total volume of influent solution; Vp: Volume of pore water in the column) of the influent solution/suspension (Fig. 2.2). A relative concentration closer to 1 refers to higher amount of As transported through the column and recovered in effluent.

2.3.4.1 As transport in the absence of HA and illite colloids

For As only experiment, As transport was very low at pH 5 (Fig. 2.2a: As). After injection of 10 pore volumes of As solution, effluent As concentration was practically zero, indicating all the injected As was retained in the column. At pH 9 (Fig. 2.2b: As), As breakthrough was much higher. The effluent As concentration reached 0.24 ± 0.08 at 2 Vp and peaked at 0.78 ± 0.01 at 10 Vp, with an overall As breakthrough of 53.3 ± 8.6 % (Table 2.2).

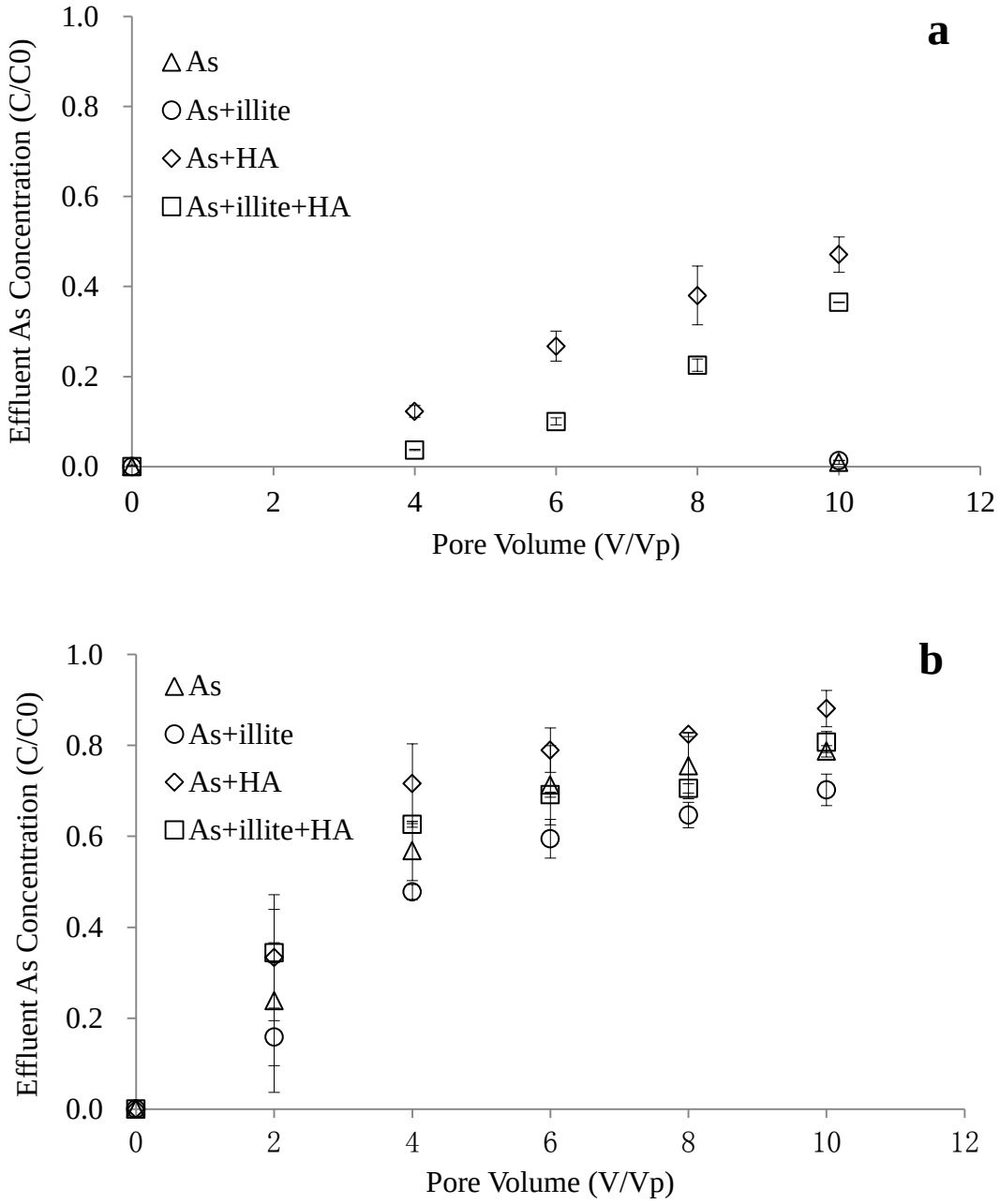

Fig. 2.2: Breakthrough curves of 10 μM As(V) through columns filled with the mixture of till and quartz sand in the absence and presence of humic acid (HA) and illite at pH 5 (a) and pH 9 (b).

In the absence of HA and mineral colloids, As transport was controlled by its adsorption to geologic media. As adsorbs to a variety of minerals and low mobility of As has been observed at low pH (Darland and Inskeep, 1997; Williams, et al., 2003).

Within the major minerals of our porous media (i.e., albite, quartz, and muscovite), no previous studies indicated apparent As adsorption to albite to our knowledge, and quartz only adsorbs minor amount of As via electrostatic interaction in the pH range of 2−10 (Xu, et al., 1988;1991), consistent with the pH_{zpc} of albite and quartz (pH_{pzc} of albite < 2, quartz < 3) (Kosmulski, 2011). Compared to albite and quartz, muscovite is able to reduce As(V) to As(III) and adsorbs As(III) (Charlet, et al., 2005; Chakraborty, et al., 2007). The minor component of Fe oxides (718 mg (as Fe) / kg) and Al oxides (211 mg (as Al) / kg) in column materials could be the dominant minerals that control As adsorption, as As forms stable surface complexes with Fe oxides (Raven, et al., 1998) and Al oxides (Xu, et al., 1988; Halter and Pfeifer, 2001). In addition, electrostatic attraction between negative charged As and positive charged Fe and Al oxides facilitated As adsorption (Xu, et al., 1991; Williams, et al., 2003).

Adsorption of As to minerals is pH dependent. Although As adsorption to albite and quartz is considered minor within the pH range of 2−10 (Xu, et al., 1988;1991; Gao, et al., 2011), muscovite shows considerable As adsorption within pH 4.2−5.5 (Chakraborty, et al., 2007). As adsorption to metal oxides is high at low pH, but decreases with increasing pH when pH is above 7 (for Fe oxides) or 9 (for Al oxides) (Xu, et al., 1988; Goldberg, 2002). pH controls adsorption by influencing As species in solution and surface property of sorbing minerals. At pH 5, arsenate is in the form of $H_2AsO_4^-$, while at pH 9 arsenate becomes more negatively charged and exists as $HAsO_4^{2-}$ (Smedley and Kinniburgh, 2002), which is less adsorbing to negatively

charged minerals. As discussed in 3.3, metal oxides in our column carried positive charges at pH 5 but negative changes at pH 9. When pH increased from 5 to 9, deprotonation of surface sites decreased As adsorption by influencing the surface complexation reaction between As and sorbing sites (Manning and Goldberg, 1997; Halter and Pfeifer, 2001). At pH 5, the positively-charged Fe and Al oxides strongly adsorbed the negative As species, resulting in low As transport. While at pH 9, Fe and Al oxides became negatively-charged, and adsorption of As became much weaker, resulting in higher As transport (Xu, et al., 1991; Goldberg, 2002). The higher As transport at higher pH observed in our experiments is consistent with previous results (Goldberg, 2002; Antelo, et al., 2005; Su, et al., 2008; Mamindy-Pajany, et al., 2011).

2.3.4.2 Effects of illite colloids

Instead of enhancing As transport, which was expected based on previous studies (Ishak, et al., 2002; Ghosh, et al., 2006; Zhang and Selim, 2007; Guo, et al., 2011), the presence of colloids had negeligeble effect on As transport at pH 5 but decreased As transport at pH 9 in our experiments. At pH 5, practically no As passed through the column in the As + illite experiment, similar to what we observed in the As only experiment (Fig. 2.2a). At pH 9, substantial As breakthrough was observed in the As + illite experiment (Fig. 2.2b), but the overall As breakthrough was lower compared to that in As only experiment (44.6 ± 3.4 % vs. 53.3 ± 8.6 %) (Table 2.2).

Colloid-facilitated As transport was suggested in previosuly studies based on the observation that higher concentration of As was found in column effluent with higher

turbidity (Puls and Powell, 1992; Zhang and Selim, 2007; Wang and Mulligan, 2009b). The magnitude of colloid-facilitated transport of sorbing contaminants such as As is controlled by the affinity of the colloids to the contaminants and the mobility of colloids. Adsorption of As to illite was proved to be moderate among different clay minerals (Manning and Goldberg, 1997; Lin and Puls, 2000). In our As + illite experiment, at pH 5, 8.5% of As was adsorbed to illite in the influent (Table 2.1). However, transport of illite was barely observed in this experiment (Fig. 2.1a: As+illite) due to high illite deposition to Fe and Al oxides. At pH 9, 4.7% of As was adsorbed to illite in the influent in our As + illite experiment (Table 2.1), and illite transport was high (Fig. 2.1b). Therefore, it was expected that As transport would be enhanced by illite. However, our results showed the opposite. The lower As transport in the presence of illite indicated higher As retention occurred on column materials. This higher As retention could be due to retention of illite-associated As when those illite colloids were retained by column materials. However, illite transport was quite high at pH 9 and all the injected illite passed through the column (Fig. 2.1b & Table 2.2). In addition to illite deposition, As desorption from illite during illite transport through the column could contribute to As immobilization in As + illite experiments. In the As spiked illite influent suspension, aqueous As (95.3% of total influent As) and illite-associated As (4.7% of total influent As) were at adsorption equilibrium, and the ratio of illite-associatd As concentration to aqueous As concentration was constrained by As distribution coefficient (K_d). During the column experiment, aqueous As

concentration in the injected As spiked illite suspension decreased due to its adsorption to column materials. This decrease in aqueous As concentration induced As desorption from illite, and the desorbed As was subsquently adsorbed to column materials. The maximum amount of As that can be immobolized by As desorption from illite in the As + illite experiments was 4.7% of the total influent As (assuming all the As adsorbed to illite was desorbed and subsquently adsorbed to column materials), much lower than the measured As immobolization of 100% − 44.6% = 55.4% (Table 2.2). The additional As immobilization (55.4% − 4.7% = 50.7% of total influent As) was attributed to adsorption of aqueous As to column materials. As indicated in our As only experiments, a substantial percentage of As (100% − 53.3% = 46.7%) was retained in the column. In our As + illite experiments, the majority (95.3%) of influent As was in aqueous phase (Table 2.1), therefore it was expected that in the As + illite experiments a similar fraction of As was adsorbed to column materials.

2.3.4.3 Effects of HA

The presence of HA increased As transport at both pH. At pH 5 (Fig. 2.2a: As+HA), As transport was much higher compared to HA-free experiments (Fig. 2.2a: As), with the overall As recovery increased from 0 to 21.3 ± 2.8 %. HA enhanced As transport also occurred at pH 9 (Fig. 2.2b: As+HA), but the impact of HA on As transport was smaller compared to that at pH 5. The overall As recovery in the As + HA experiments and the As only experiments was 62.1 ± 6.0 % and 53.3 ± 8.6 %,

respectively (Table 2.2).

Enhanced As mobility in the presecne of NOM has been reported (Wang and Mulligan, 2009b;2009a; Sharma, et al., 2011). One mechanism for the increased As transport in the presence of HA is the competition between HA and As for binding sites on column materials (Fe and Al oxides, as well as main minerals) (Redman, et al., 2002). As discussd in 2.3.4.1, As adsorbs to Fe and Al oxides through surface complexation (Xu, et al., 1988; Raven, et al., 1998; Halter and Pfeifer, 2001) and electrostatic interaction (Xu, et al., 1991; Williams, et al., 2003), while HA adsorbs to Fe and Al oxides by electrostatic interactions, association via aliphatic/aromatic carbon, and ligand exchange or H-bonding with carboxyl/hydroxyl functional groups (discussed in 2.3.3) (Tipping, 1981; Gu, et al., 1994; Fein, et al., 1999; Borggaard, et al., 2005; Yang, et al., 2013). HA also adsorbs to the main minerals in our column (i.e. albite, quartz, and muscovite): HA adsorbs to quartz via weak van der Waals and electrostatic interaction (Kubicki, et al., 1999; Jada, et al., 2006), and adsorbs to the basal plane of muscovite (Plaschke, et al., 1999). Adsorption of HA to column materials occupied some of the sorption sites for As and increased As transport. Another mechanism for increased As transport involves formation of aqueous complexes between HA and As (Ko, et al., 2004; Buschmann, et al., 2006). Although the predominant As species ($H_2AsO_4^-$ and $HAsO_4^{2-}$) and HA were both negatively charged, As can form aqueous complexs with HA through the combination of positive arsenate center and negative phenolate entity provided by HA (Buschmann, et al.,

2006). Another potential mechanism of the HA-enhanced As transport is reduction of As(V) by NOM to less adsorbing and more mobile As(III). (Smedley and Kinniburgh, 2002). However, the reduction of As(V) to As(III) requires a much longer time than the duration of our experiment (Dobran and Zagury, 2006). Therefore, As(V) reduction to As(III) is unlikely in our experiments.

2.3.4.4 As transport in the presence of both HA and illite colloids

In the presence of both HA and illite colloids, at pH 5, the overall As recovery was 11.3 ± 0.5 % (Table 2.2). This recovery was lower than that of As + HA experiment (21.3 ± 2.8 %), but higher than that of As only and As + illite experiments (0 recovery). At pH 9, As recovery in the presence of both HA and illite was 55.4 ± 1.1 % (Table 2.2), practically the same as the recovery of the As only experiments (53.3 ± 8.6 %), but lower than that in the As + HA experiment (62.1 ± 6.0 %), and higher than that in the As + illite experiment (44.6 ± 3.4 %).

Although illite transport was enhanced in the presence of HA (especially at pH 5), this increase in illite trasnport is unlikely to increase As transport. At both pH 5 and 9, adsorption of As to illite was very weak in the presence of HA (Table 2.1), making illite facilitated transport of As unimportant (simialr to what we discussed in 2.3.4.2). At pH 5 the higher transport of As in the As + illite + HA experiments compared to that in As only and As + illite experiments, and at pH 9 the higher As transport in the As + illite + HA experiments compared to that in the As + illite experiments is presumably due to HA-enhanced As transport (discussed in 2.3.4.3). At pH 9, As

transport in the As + illite + HA experiments was the same as that in the As only experiments, indicating the effects of competition between HA and As for sorptive sites on column materials, formation of aqueous HA-As complexes, and illite colloids on As transport was weak and negligible. At both pH 5 and 9, transport of As in the As + illite + HA experiments was lower compared to that in the As + HA experiemnts. This is caused by HA adsorption to illite in the influent (discussed in 2.3.2). HA adsorption to illite colloids reduced the amount of aqueous HA in the influent (Filip and Alberts, 1994; Liu and Gonzalez, 1999). Lower aqueous HA concentration suggested less HA available to (i) compete with As for sorptive sites on column materials, and (ii) form As-HA aqueous complexes, leading to lower As transport.

2.4 Conclusions and Implications

Both illite colloids and HA influence As transport in water-saturated sand columns, but through different mechanisms and leading to different results. At low pH, illite colloids had minor influence on As transport due to the low mobility of colloids. At high pH, illite colloids decreased As transport due to As desorption from illite colloids. At both low and high pH, HA not only increased illite colloid transport, but also increased As transport via (i) competition with As for adsorptive sites on column materials and (ii) formation of aqueous As-HA complexes. In the presence of both illite colloids and HA, As transport was normally increased with respect to HA-free systems (i.e., As only, and As + illite systems), due to HA-enhanced As transport. However, As transport was lower in systems with both illite colloids and HA

compared to that in systems with HA but no illite. HA adsorption to illite colloids can effectively decrease aqueous phase HA concentration, making HA-enhanced As transport less pronounced. In natural environments, mineral colloids and natural organic matter usually co-exist. Therefore, it is necessary to consider the combined effects of mineral colloids and natural organic matter when assessing As transport in real subsurface environments.

2.5 References

Akbour, R. A., Douch, J., Hamdani, M., and Schmitz, P. (2002). Transport of kaolinite colloids through quartz sand: Influence of humic acid, Ca2+, and trace metals. *Journal of Colloid and Interface Science, 253*(1), 1-8.

Antelo, J., Arce, F., Avena, M., Fiol, S., Lopez, R., and Macias, F. (2007). Adsorption of a soil humic acid at the surface of goethite and its competitive interaction with phosphate. *Geoderma, 138*(1-2), 12-19.

Antelo, J., Avena, M., Fiol, S., Lopez, R., and Arce, F. (2005). Effects of pH and ionic strength on the adsorption of phosphate and arsenate at the goethite-water interface. *Journal of Colloid and Interface Science, 285*(2), 476-486.

Arnarson, T. S., and Keil, R. G. (2000). Mechanisms of pore water organic matter adsorption to montmorillonite. *Marine Chemistry, 71*(3–4), 309-320.

Baumann, T., Fruhstorfer, P., Klein, T., and Niessner, R. (2006). Colloid and heavy metal transport at landfill sites in direct contact with groundwater. *Water Research, 40*(14), 2776-2786.

Borggaard, O. K., Raben-Lange, B., Gimsing, A. L., and Strobel, B. W. (2005). Influence of humic substances on phosphate adsorption by aluminium and iron oxides. *Geoderma, 127*(3–4), 270-279.

Boyle, D. R., Turner, R. J. W., and Hall, G. E. M. (1998). Anomalous arsenic concentrations in groundwaters of an island community, Bowen Island, British Columbia. *Environmental Geochemistry and Health, 20*(4), 199-212.

Buschmann, J., Kappeler, A., Lindauer, U., Kistler, D., Berg, M., and Sigg, L. (2006). Arsenite and arsenate binding to dissolved humic acids: Influence of pH, type of humic acid, and aluminum. *Environmental Science & Technology, 40*(19), 6015-6020.

Chakraborty, S., Wolthers, M., Chatterjee, D., and Charlet, L. (2007). Adsorption of arsenite and arsenate onto muscovite and biotite mica. *Journal of Colloid and Interface Science, 309*(2), 392-401.

Charlet, L., Chakraborty, S., Varma, S., Tournassat, C., Wolthers, M., Chatterjee, D., and Ross, G. R. (2005). Adsorption and heterogeneous reduction of arsenic at the phyllosilicate-water interface. In P. A. Oday, D. Vlassopoulos, Z. Meng & L. G. Benning (Eds.), *Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation* (Vol. 915, pp. 41-+). Washington: Amer Chemical Soc.

Chen, G. X., Liu, X. Y., and Su, C. M. (2012). Distinct Effects of Humic Acid on Transport and Retention of TiO2 Rutile Nanoparticles in Saturated Sand Columns. *Environmental Science & Technology, 46*(13), 7142-7150.

Chen, Z. R., Cai, Y., Liu, G. L., Solo-Gabriele, H., Snyder, G. H., and Cisar, J. L. (2008). Role of soil-derived dissolved substances in arsenic transport and transformation in laboratory experiments. *Science of the Total Environment, 406*(1-2), 180-189.

Cheng, H. F., Hu, Y. N., Luo, J., Xu, B., and Zhao, J. F. (2009). Geochemical

processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems. *Journal of Hazardous Materials, 165*(1-3), 13-26.

Cornu, S., Saada, A., Breeze, D., Gauthier, S., and Baranger, P. (1999). The influence of organic complexes on arsenic adsorption onto kaolinites. *Comptes Rendus De L Academie Des Sciences Serie Ii Fascicule a-Sciences De La Terre Et Des Planetes, 328*(10), 649-654.

Darland, J. E., and Inskeep, W. P. (1997). Effects of pH and phosphate competition on the transport of arsenate. *Journal of Environmental Quality, 26*(4), 1133-1139.

Datta, A., Sanyal, S. K., and Saha, S. (2001). A study on natural and synthetic humic acids and their complexing ability towards cadmium. *Plant and Soil, 235*(1), 115-125.

Dobran, S., and Zagury, G. J. (2006). Arsenic speciation and mobilization in CCA-contaminated soils: Influence of organic matter content. *Science of the Total Environment, 364*(1-3), 239-250.

Fairhurst, A. J., Warwick, P., and Richardson, S. (1995). The influence of humic acid on the adsorption of europium onto inorganic colloids as a function of pH. *Colloids and Surfaces a-Physicochemical and Engineering Aspects, 99*(2-3), 187-199.

Fein, J. B., Boily, J.-F., Güçlü, K., and Kaulbach, E. (1999). Experimental study of humic acid adsorption onto bacteria and Al-oxide mineral surfaces. *Chemical Geology, 162*(1), 33-45.

Filip, Z., and Alberts, J. J. (1994). Adsorption and transformation of salt marsh related humic acids by quartz and clay minerals. *Science of the Total Environment, 153*(1–2), 141-150.

Gao, X. B., Wang, Y. X., Hu, Q. H., and Su, C. L. (2011). Effects of anion competitive adsorption on arsenic enrichment in groundwater. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering, 46*(5), 471-479.

Ghosh, A., Mukiibi, M., Sáez, A. E., and Ela, W. P. (2006). Leaching of arsenic from granular ferric hydroxide residuals under mature landfill conditions. *Environmental Science and Technology, 40*(19), 6070-6075.

Giasuddin, A. B. M., Kanel, S. R., and Choi, H. (2007). Adsorption of humic acid onto nanoscale zerovalent iron and its effect on arsenic removal. *Environmental Science & Technology, 41*(6), 2022-2027.

Goldberg, S. (2002). Competitive Adsorption of Arsenate and Arsenite on Oxides and Clay Minerals. *Soil Science Society of America Journal, 66*(2), 413-421.

Gradusov, B. P. (1974). A tentative study of clay mineral distribution in soils of the world. *Geoderma, 12*(1–2), 49-55.

Greenland, D. J. (1971). Interactions between humic and fulvic acids and clays. *Soil Science, 111*(1), 34-&.

Grolimund, D., Borkovec, M., Barmettler, K., and Sticher, H. (1996). Colloid-facilitated transport of strongly sorbing contaminants in natural porous

media: A laboratory column study. *Environmental Science & Technology, 30*(10), 3118-3123.

Gu, B. H., Schmitt, J., Chen, Z. H., Liang, L. Y., and McCarthy, J. F. (1994). Adsorption and desorption of natural organic matter on iron-oxide: mechanisms and models. *Environmental Science & Technology, 28*(1), 38-46.

Gu, X., and Evans, L. J. (2007). Modelling the adsorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) onto Fithian illite. *Journal of Colloid and Interface Science, 307*(2), 317-325.

Guo, H. M., Zhang, B., Yang, S. Z., Li, Y., Stuben, D., Norra, S., and Wang, J. J. (2009). Role of colloidal particles for hydrogeochemistry in As-affected aquifers of the Hetao Basin, Inner Mongolia. *Geochemical Journal, 43*(4), 227-234.

Guo, H. M., Zhang, B., and Zhang, Y. (2011). Control of organic and iron colloids on arsenic partition and transport in high arsenic groundwaters in the Hetao basin, Inner Mongolia. *Applied Geochemistry, 26*(3), 360-370.

Halter, W. E., and Pfeifer, H.-R. (2001). Arsenic(V) adsorption onto α-Al2O3 between 25 and 70 ℃. *Applied Geochemistry, 16*(7–8), 793-802.

Haque, S., and Johannesson, K. H. (2006). Arsenic concentrations and speciation along a groundwater flow path: The Carrizo Sand aquifer, Texas, USA. *Chemical Geology, 228*(1–3), 57-71.

Hossain, M. S., and Islam, M. R. (2008). Experimental and numerical modeling of

arsenic transport in limestone. *Energy Sources Part a-Recovery Utilization and Environmental Effects, 30*(13), 1189-1201.

Hu, L. G., Diez-Rivas, C., Hasan, A. R., Solo-Gabriele, H., Fieber, L., and Cai, Y. (2010). Transport and interaction of arsenic, chromium, and copper associated with CCA-treated wood in columns of sand and sand amended with peat. *Chemosphere, 78*(8), 989-995.

Ishak, C. F., Seaman, J. C., Miller, W. P., and Sumner, M. (2002). Contaminant mobility in soils amended with fly ash and flue-gas gypsum: Intact soil cores and repacked columns. *Water, Air, and Soil Pollution, 134*(1-4), 287-305.

Jada, A., Ait Akbour, R., and Douch, J. (2006). Surface charge and adsorption from water onto quartz sand of humic acid. *Chemosphere, 64*(8), 1287-1295.

Johnson, P. R., Sun, N., and Elimelech, M. (1996). Colloid transport in geochemically heterogeneous porous media: Modeling and measurements. *Environmental Science & Technology, 30*(11), 3284-3293.

Ko, I., Kim, J.-Y., and Kim, K.-W. (2004). Arsenic speciation and sorption kinetics in the As–hematite–humic acid system. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 234*(1–3), 43-50.

Kosmulski, M. (2011). The pH-dependent surface charging and points of zero charge: V. Update. *Journal of Colloid and Interface Science, 353*(1), 1-15.

Kostic, I., Andelkovic, T., Nikolic, R., Bojic, A., Purenovic, M., Blagojevic, S., and Andelkovic, D. (2011). Copper(II) and lead(II) complexation by humic acid

and humic-like ligands. *Journal of the Serbian Chemical Society, 76*(9), 1325-1336.

Kretzschmar, R., Borkovec, M., Grolimund, D., and Elimelech, M. (1999). Mobile subsurface colloids and their role in contaminant transport. *Advances in Agronomy, Vol 66, 66*, 121-193.

Kubicki, J. D., Schroeter, L. M., Itoh, M. J., Nguyen, B. N., and Apitz, S. E. (1999). Attenuated total reflectance Fourier-transform infrared spectroscopy of carboxylic acids adsorbed onto mineral surfaces. *Geochimica Et Cosmochimica Acta, 63*(18), 2709-2725.

Laegdsmand, M., de Jonge, L. W., and Moldrup, P. (2005). Leaching of colloids and dissolved organic matter from columns packed with natural soil aggregates. *Soil Science, 170*(1), 13-27.

Lin, Z., and Puls, R. W. (2000). Adsorption, desorption and oxidation of arsenic affected by clay minerals and aging process. *Environmental Geology, 39*(7), 753-759.

Liu, A. G., and Gonzalez, R. D. (1999). Adsorption/desorption in a system consisting of humic acid, heavy metals, and clay minerals. *Journal of Colloid and Interface Science, 218*(1), 225-232.

Mamindy-Pajany, Y., Hurel, C., Marmier, N., and Roméo, M. (2011). Arsenic (V) adsorption from aqueous solution onto goethite, hematite, magnetite and zero-valent iron: Effects of pH, concentration and reversibility. *Desalination,*

281(0), 93-99.

Manning, B. A., and Goldberg, S. (1997). Adsorption and stability of arsenic(III) at the clay mineral-water interface. *Environmental Science & Technology, 31*(7), 2005-2011.

McCarthy, J. F., and McKay, L. D. (2004). Colloid mobilization and transport in groundwater. *Vadose Zone Journal, 3*(2), 326-337.

Metreveli, G., Abbt-Braun, G., and Frimmel, F. H. (2010). Influence of NOM on the Mobility of Metal(loid)s in Water-Saturated Porous Media. *Aquatic Geochemistry, 16*(1), 85-100.

Mohapatra, D., Mishra, D., Chaudhury, G. R., and Das, R. P. (2007). Arsenic(V) adsorption mechanism using kaolinite, montmorillonite and illite from aqueous medium. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering, 42*(4), 463-469.

Paktunc, D., Foster, A., and Laflamme, G. (2003). Speciation and characterization of arsenic in Ketza River mine tailings using x-ray absorption spectroscopy. *Environmental Science & Technology, 37*(10), 2067-2074.

Plaschke, M., Romer, J., Klenze, R., and Kim, J. I. (1999). In situ AFM study of sorbed humic acid colloids at different pH. *Colloids and Surfaces a-Physicochemical and Engineering Aspects, 160*(3), 269-279.

Polubesova, T., and Nir, S. (1999). Modeling of organic and inorganic cation sorption by illite. *Clays and Clay Minerals, 47*(3), 366-374.

Puls, R. W., and Powell, R. M. (1992). Transport of inorganic colloids through natural aquifer material: Implications for contaminant transport. *Environmental Science and Technology, 26*(3), 614-621.

Ransom, B., and Helgeson, H. C. (1993). Compositional end members and thremodynamic components of illite and dioctahedral aluminous smectite solid-solutions. *Clays and Clay Minerals, 41*(5), 537-550.

Raven, K. P., Jain, A., and Loeppert, R. H. (1998). Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. *Environmental Science & Technology, 32*(3), 344-349.

Redman, A. D., Macalady, D. L., and Ahmann, D. (2002). Natural organic matter affects arsenic speciation and sorption onto hematite. *Environmental Science & Technology, 36*(13), 2889-2896.

Saiers, J. E. (2002). Laboratory observations and mathematical modeling of colloid-facilitated contaminant transport in chemically heterogeneous systems. *Water Resources Research, 38*(4).

Saiers, J. E., and Hornberger, G. M. (1999). The influence of ionic strength on the facilitated transport of cesium by kaolinite colloids. *Water Resources Research, 35*(6), 1713-1727.

Schmitt, D., Saravia, F., Frimmel, F. H., and Schuessler, W. (2003). NOM-facilitated transport of metal ions in aquifers: importance of complex-dissociation kinetics and colloid formation. *Water Research, 37*(15), 3541-3550.

Serpa, C., Batterson, M. and Guzzwell, K. . (2009). The influence of bedrock and mineral occurrences on Arsenic concentrations in groundwater wells in the Gander Bay Area, Newfoundland. *Current Research (2009) Newfoundland and Labrador Department of Natural Resources Geological Survey*(Report 09-1), 315-337.

Sharma, P., Rolle, M., Kocar, B., Fendorf, S., and Kappler, A. (2011). Influence of Natural Organic Matter on As Transport and Retention. *Environmental Science & Technology, 45*(2), 546-553.

Smedley, P. L., and Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry, 17*(5), 517-568.

Su, T. Z., Guan, X. H., Gu, G. W., and Wang, J. M. (2008). Adsorption characteristics of As(V), Se(IV), and V(V) onto activated alumina: Effects of pH, surface loading, and ionic strength. *Journal of Colloid and Interface Science, 326*(2), 347-353.

Tang, X. Y., and Weisbrod, N. (2009). Colloid-facilitated transport of lead in natural discrete fractures. *Environmental Pollution, 157*(8-9), 2266-2274.

Tatalovich, M. E., Lee, K. Y., and Chrysikopoulos, C. V. (2000). Modeling the transport of contaminants originating from the dissolution of DNAPL pools in aquifers in the presence of dissolved humic substances. *Transport in Porous Media, 38*(1-2), 93-115.

Tessier, A., Campbell, P. G., and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical chemistry, 51*(7), 844-851.

Tindale, K., Patel, P., and Wallschlager, D. (2011). Colloidal arsenic composition from abandoned gold mine tailing leachates in Nova Scotia, Canada. *Applied Geochemistry, 26*, S260-S262.

Tipping, E. (1981). The adsorption of aquatic humic substances by iron oxides. *Geochimica Et Cosmochimica Acta*, *45*(2), 191-199.

Tombacz, E., Dobos, A., Szekeres, M., Narres, H. D., Klumpp, E., and Dekany, I. (2000). Effect of pH and ionic strength on the interaction of humic acid with aluminium oxide. *Colloid and Polymer Science*, *278*(4), 337-345.

Wang, S., and Mulligan, C. N. (2006). Occurrence of arsenic contamination in Canada: Sources, behavior and distribution. *Science of the Total Environment, 366*(2-3), 701-721.

Wang, S. L., and Mulligan, C. N. (2009a). Effect of natural organic matter on arsenic mobilization from mine tailings. *Journal of Hazardous Materials, 168*(2-3), 721-726.

Wang, S. L., and Mulligan, C. N. (2009b). Enhanced mobilization of arsenic and heavy metals from mine tailings by humic acid. *Chemosphere, 74*(2), 274-279.

Wang, T., Liu, W., Xiong, L., Xu, N., and Ni, J. R. (2013). Influence of pH, ionic strength and humic acid on competitive adsorption of Pb(II), Cd(II) and Cr(III)

onto titanate nanotubes. *Chemical Engineering Journal, 215*, 366-374.

Williams, L. E., Barnett, M. O., Kramer, T. A., and Melville, J. G. (2003). Adsorption and transport of arsenic(V) in experimental subsurface systems. *Journal of Environmental Quality, 32*(3), 841-850.

Xu, H., Allard, B., and Grimvall, A. (1988). Influence of pH and organic substance on the adsorption of As(V) on geologic materials. *Water, Air, and Soil Pollution, 40*(3-4), 293-305.

Xu, H., Allard, B., and Grimvall, A. (1991). Effects of acidification and natural organic materials on the mobility of arsenic in the environment. *Water Air and Soil Pollution, 57-8*, 269-278.

Yang, Y., Saiers, J. E., and Barnett, M. O. (2013). Impact of Interactions between Natural Organic Matter and Metal Oxides on the Desorption Kinetics of Uranium from Heterogeneous Colloidal Suspensions. *Environmental Science & Technology, 47*(6), 2661-2669.

Yang, Y., Saiers, J. E., Xu, N., Minasian, S. G., Tyliszczak, T., Kozimor, S. A., Shuh, D. K., and Barnett, M. O. (2012). Impact of Natural Organic Matter on Uranium Transport through Saturated Geologic Materials: From Molecular to Column Scale. *Environmental Science & Technology, 46*(11), 5931-5938.

Zhang, H., and Selim, H. M. (2007). Colloid mobilization and arsenite transport in soil columns: Effect of ionic strength. *Journal of Environmental Quality, 36*(5), 1273-1280.

Zhang, L., Yu, X., Zhang, H., Chen, E., and Dong, T. (2013). Impact of environmental conditions on the sorption behavior of 60Co(II) on illite. *Journal of Radioanalytical and Nuclear Chemistry, 295*(2), 1473-1485.

Zhang, W., Morales, V. L., Cakmak, M. E., Salvucci, A. E., Geohring, L. D., Hay, A. G., Parlange, J. Y., and Steenhuis, T. S. (2010). Colloid Transport and Retention in Unsaturated Porous Media: Effect of Colloid Input Concentration. *Environmental Science & Technology, 44*(13), 4965-4972.

Chapter 3. Influence of Mineral Colloids and Natural Organic Matter on Uranium Transport in Water-Saturated Geologic Materials

Abstract

Numerous studies have shown that uranium (U) transport in subsurface environments can be substantially influenced by waterborne mineral colloids and natural organic matter. However, the combined effects of mineral colloids and natural organic matter on U transport are not clear. This gap in knowledge prevents us from accurate assessment of U migration in subsurface environments where mineral colloids and natural organic matter often co-exist. The objectives of this study are to: (i) quantify U transport under conditions when both mineral colloids and humic acid (HA) (a proxy for natural organic matter) are present, and (ii) elucidate important geochemical processes that control colloids- and HA-mediated U transport. U-spiked solutions/suspensions were passed through water-saturated columns packed with natural sediment and quartz sand, and U and colloid concentrations in column effluent were determined. We found that HA at both pH 5 and 9 promoted U transport due to (i) competition with U for adsorptive sites on geologic materials and (ii) formation of aqueous U-HA complexes. Illite colloids by itself had no influence on U transport at pH 5 due to low mobility of colloids. At pH 9, however, illite colloids decreased U transport due to U desorption from illite colloids. High U transport occurred when both illite colloids and HA were present, which was attributed to enhanced U adsorption to illite colloids via formation of ternary illite-HA-U surface complexes,

and enhanced illite transport due to HA attachment to illite and geologic media. When evaluating U transport in real subsurface environments the combined effects of mineral colloids and HA must be considered.

Keywords: Humic acid, illite colloid, U transport, column experiment, adsorption, deposition

3.1 Introduction

Uranium (U) is a naturally occurring radionuclide that can be found in rock, water, and soil. U in groundwater is derived from natural interactions between U-bearing minerals and groundwater as well as processing of nuclear fuels and materials (Jerden Jr and Sinha, 2006; Dresel, et al., 2011). Once released to groundwater, U can migrate with groundwater flow and cause contamination in drinking water aquifers (Kronfeld, et al., 2004; Babu, et al., 2008). To assess the extent of U contamination in groundwater and the risk to human health from U exposure by consuming contaminated groundwater, it is important to understand how U transports in subsurface environment.

Adsorption of dissolved uranium to aquifer materials such as iron oxides can significantly reduce U transport (Gabriel, et al., 1998; Barnett, et al., 2000; Cheng, et al., 2007). In contrast, the ubiquitous presence of submicron-sized particles such as mineral colloids and natural organic matters (NOM) (e.g., humic substances) in groundwater can enhance U transport (Kaplan, et al., 1994; Bekhit and Hassan, 2007; Crancon, et al., 2010). Mineral colloids and natural organic matter have large surface area that contain highly reactive functional groups, therefore these small particles have high affinity to many dissolved contaminants (Baek and Pitt, 1996; Grolimund, et al., 1996; Kalbitz and Wennrich, 1998; Schmitt, et al., 2003; Kretzschmar and Schafer, 2005). The ability of colloids and NOM to promote contaminant transport depends on the mobility of these small particles and their ability to retain contaminants. NOM and

colloidal particles were found to strongly adsorb U (Lienert, et al., 1994; Lenhart, et al., 2000; Crancon, et al., 2010; Chau, et al., 2011) and promote U transport in groundwater (Kaplan, et al., 1994; Kim, et al., 1994; Bekhit and Hassan, 2007). Although extensive studies on colloid-facilitated U transport (e.g., Porcelli, et al., 1997; Andersson, et al., 2001) and NOM-facilitated U transport (Artinger, et al., 2002; Sachs, et al., 2006; Mibus, et al., 2007; Yang, et al., 2012) have been carried out, fewer studies investigated the combined effects of NOM and mineral colloids on U transport. In natural environment, NOM, mineral colloids and contaminants usually co-exist and interact with one another via a suite of geochemical processes (Yang, et al., 2013). For instance, NOM can (i) form aqueous complexes with contaminants (Datta, et al., 2001; Schmitt, et al., 2003; Metreveli, et al., 2010; Kostic, et al., 2011), and (ii) compete with contaminants for surface sites on aquifer materials (Antelo, et al., 2007; Giasuddin, et al., 2007; Wang, et al., 2013). At the same time, by attaching to mineral colloids, NOM can (i) alter (either enhance or reduce) mineral colloids' ability to adsorb contaminants (Yang, et al., 2013), and (ii) enhance the mobility of mineral colloids (Yoshida and Suzuki, 2008; Morales, et al., 2011). The overall effects of NOM and mineral colloids on U transport due to these diverse and concomitant processes are difficult to predict, because these processes are additive under certain conditions, but become competitive under other conditions depending on water chemistry and chemical compositions of NOM, colloids, and contaminants. Experimental studies of the combined effects of mineral colloids and NOM on U

transport will provide valuable data for evaluating U transport in real subsurface environments.

The objectives of this study were to determine the combined effects of mineral colloids and NOM on U transport, and elucidate the important geochemical processes that control U transport in the presence of mineral colloids and NOM. Illite was used as a representative mineral colloid due to its abundance in natural subsurface environment (Gradusov, 1974; Ransom and Helgeson, 1993). Humic acid, which is a major component of NOM, was used as a proxy for NOM in our study. U and illite transport was investigated by injecting U-containing solution/suspension into water-saturated columns packed with a mixture of natural sediment and quartz sand, and analyzing U and illite concentration in column effluent. Eight column experiments, distinguished based on the composition of the U-containing solution (U only, U + illite, U + HA, and U + HA + illite) and solution pH (pH 5 and pH 9), were performed to determine the influence of mineral colloids and NOM on U transport.

3.2 Materials and Methods

3.2.1 Preparation of influent illite colloid suspensions and solutions

Nitric acid (HNO_3), sodium hydroxide (NaOH), sodium nitrate ($NaNO_3$), and 1000 mg/L U stock solution ($UO_2(NO_3)_2 \cdot 6H_2O$, catalog # 82026-084) were all certified ACS grade and purchased from VWR. Humic acid (HA) purchased from Alfa Aesar (catalog # 41747-14) was used without pre-treatment. Illite (IMt-2) was

purchased from The Clay Mineral Society and its major chemical composition (mass %) was: SiO_2: 49.3 Al_2O_3: 24.25, TiO_2: 0.55, Fe_2O_3: 7.32, FeO: 0.55, MnO: 0.03, MgO: 2.56, CaO: 0.43. All the solutions and suspensions were prepared with nano-pure water.

Influent illite colloid suspension was prepared from dilution of a stock suspension. Illite colloid stock suspension was prepared following the method of Saiers and Hornberger (1999). Four grams (4.0 g) of illite powder was suspended in 1000 mL nano-pure water in a high-density polyethylene bottle. After vigorous shaken, the suspension was dispersed for 30 mins in an ultrasonic bath. Then the suspension was transferred to a flask and let stand for 24 hours before the supernatant was transferred to another high-density polyethylene bottle. The supernatant was used as our illite stock suspension. Illite concentration in the stock suspension was measured gravimetrically by filtering 100 mL of the suspension through a 0.1μm polyethersulfone membrane filter (Pall Life Sciences). The filter was oven dried at 60 ℃ before and after the filtration, and the difference between the weights of the filter was considered as the mass of the colloids. The illite stock suspension was well mixed and diluted to a desired concentration of 100 mg/L 24 hours before used in column experiments.

Four types of U-spiked influent solutions/suspensions were prepared at both pH 5 and pH 9 with the same background electrolyte (0.01 M $NaNO_3$): U only, U + illite, U + HA, and U + HA + illite by directly adding HA and diluting stock solution of U and

illite stock suspension (Table 3.1). Final concentrations of U, HA, and illite colloids in the U-spiked influents were 1 mg/L, 12 mg (organic carbon)/L, and 100 mg/L. In order to pack and precondition the columns, U-free background solution with the same electrolyte (0.01 M $NaNO_3$) as the U-spiked influent was prepared. HA (12 mg C/L) was present in the background solution for experiments of U-spiked influent with HA (U + HA, U + HA + illite), and no HA was present in the background solution for U-spiked influent without HA (U only, U + illite). All the experimental solutions and suspensions (including background solutions) were adjusted to desired pH (5 or 9) using HNO_3 and NaOH before used in column experiments.

3.2.2 Characterization of influent illite suspensions

Zeta potential and particle size of each U and illite colloid-spiked influent suspension were determined using a Zetasizer Nano-ZS (Malvern). Membrane filtration was conducted to U and illite-spiked influent suspensions to quantify the association between U and illite colloids. Well-mixed illite-spiked U influent suspension was filtered through a 0.1 μm polyethersulfone membrane filter (Pall Life Sciences) with a vacuum filtration unit (VWR). The influentt suspension as well as the filtrate were colloected and analyzed for U concentration following the method described below (in 3.2.5). The difference between the U concentration in the influent and filtrate was considered as U adsorbed to illite colloids.

3.2.3 Column materials

The columns were packed with a mixed material of natural sediment and pure quartz sand. The natural sediment was collected from Avondale, a town located in Avalon Peninsula in Eastern Newfoundland. The sediment was air dried, gently ground to smaller particles, and passed a serial of sieves. The sieved fraction with a grain size range between 0.25 and 0.60 mm was collected. Mineral composition of the sieved sediment was determined with X-ray diffraction (XRD), and concentrations of Fe oxides and Al (hydro)oxides in the sieved sediment were determined using a sequential extraction method (Tessier, et al., 1979). The quartz sand (VWR, catalog # 71008-394) is mineralogically pure and contains >99.7% of SiO_2, <0.02% of Fe_2O_3, and <0.05% of Al_2O_3. Before use, the quartz sand was washed with nano-pure water, air dried, and sieved to grain sizes between 0.25 and 0.60 mm. The above pretreated natural sediment and quartz sand with the same size range were well mixed at a mass ration of 4:1 (quartz sand to sediment) and used to pack columns in our study.

3.2.4 Column experiments

Eight column experiments were conducted, distinguished by the pH and different composition of the U-spiked influent (Table 3.1), and duplicates were conducted for all of the eight experiments. A Kontes ChromaFlex™ chromatography glass column (2.5 cm inner diameter, 15 cm length) was used in the column experiments. For each experiment, a column was wet-packed by slowly pouring the well-mixed column materials (described in 3.2.3) into the column with simultaneous tapping to maintain the uniformity and remove any air bubbles. Dry mass of the column material and

volume of the solution used to pack the column was recorded. The average dry mass of the column material and average volume of background solution used to pack the column (i.e., pore volume) was 127 g and 23 cm^3 respectively, corresponding to a bulk density of 1.73 g/cm^3 and a porosity of 0.31.

Two phases were run for each column experiment: (1) ~18 hours' column precondition phase with background solution until the pH of effluent (from the top of the column) was stable, followed by (2) injection phase with 10 pore volumes (Vp) of U-spiked influent solution or suspension. A peristaltic pump (Masterflex, Cole-Parmer Instruments) was used to continuously inject different experimental solution/suspension to the column with upward flow based at a specific discharge of 0.66 cm/min during the two phases. The effluent from the top of the column was sampled with a fraction collector (CF-2, Spectrum Chromatography) for analyses of U and illite concentrations.

3.2.5 Analytical methods

The concentration of U and other elements in the influent and effluent samples was determined by ICP-MS (inductively coupled plasma mass spectrometry). One gram (1.0000 g) of well mixed influent or effluent samples was transferred to a Teflon screw cap jar, mixed with 1 mL of 16 mol/L HNO_3 and kept on a hot plate (70 ℃) for 24 hours to dissolve all the U and particles in the samples. Then the solutions was transferred to a clean tube and diluted to 20.00 g before sent to ICP-MS. Our tests showed that this method was able to recover 104.4 $\pm$ 4.3 % of U even in the presence

of 100 mg/L illite colloid. ICP-MS measured elemental Fe concentration was used to quantify illite colloids with a calibration curve made with a series of suspensions containing known concentrations of illite colloids and Fe concentrations (Grolimund, et al., 1996).

3.3 Results and Discussion

3.3.1 Mineralogical and chemical properties of natural sediment

The natural sediment used as column material mainly consists of albite (50.5% mass), quartz (34.9% mass) and muscovite (14.7% mass) according to our X-ray diffraction (XRD) results. Metal (Fe and Al) oxides were not detected by XRD, indicating their concentration was below the detection limit of XRD analysis (~5% of total mass). Sequential extraction and elemental analysis showed the concentration of Fe and Al oxides are 3592 mg (as Fe) /kg and 1057 mg (as Al) /kg respectively.

3.3.2 Zeta potential and particle size of illite, U and HA adsorption to illite in influent suspension

In the absence of HA, illite colloids were negatively charged at both pH 5 and 9, (Table 3.1). At pH 9, zeta potential of illite was more negative compared to that at pH 5 (-42.4 mV vs. -33 mV). The above results were consistent with the point of zero charge of illite (pH_{pzc} = 2.5) (Kosmulski, 2011). In the presence of HA, zeta potential of illite colloids became slightly more negative at both pH 5 and 9, indicating adsorption of negatively charged HA to illite.

The average diameter of illite colloids was in the range of 250~300 nm. At pH 5, the size of illite colloids was not affected by HA, while at pH 9, the measured size of illite was slightly lower in the presence of HA (281.8 ± 3.0 nm vs. 254.0 ± 13.2 nm) (Table 3.1). In our filtration procedure, the pore size of the filter membrane was 100 nm, much smaller than the size of illite colloids, therefore the membrane was expected to retain the majority of the illite, and U in the filtrate represents aqueous U (i.e., U not associated with illite).

Table 3.1: Conditions of column experiments and properties of illite colloids.

pH	Influent	Zeta Potential (mV)	Particle Size (d. nm)	% U associated with illite
5	U	NA	NA	NA
	U + illite	-33.0 ± 1.8	297.2 ± 17.8	19.0 ± 4.9 %
	U + HA	NA	NA	NA
	U + HA + illite	-37.1 ± 1.4	294.4 ± 14.4	87.4 ± 0.8 %
9	U	NA	NA	NA
	U + illite	-42.5 ± 0.3	281.8 ± 3.0	33.2 ± 4.0 %
	U + HA	NA	NA	NA
	U + HA + illite	-43.9 ± 0.1	254.0 ± 13.2	39.6 ± 3.6 %

In the absence of HA, 19.0 ± 4.9 % U in our U-spiked influent was associated with illite at pH 5, at pH 9, 33.2 ± 4.0 % of U in the influent was associated with illite (Table 3.1). At low pH, U adsorption to clay minerals is weak and mainly due to U reaction with fixed-charge sites on the basal planes of clay minerals, while at high pH, U is adsorbed to metal-oxide like edge sites (e.g. Al-OH, Si-OH) on clay minerals (McKinley, et al., 1995; Chisholm-Brause, et al., 2004; Bachmaf and Merkel, 2011).

The presence of HA increased U adsorption to 87.4 ± 0.8 % at pH 5 and to 39.6 ± 3.6 % at pH 9 (Table 3.1). The increased U adsorption to illite in the presence of HA was attributed to adsorption of HA to illite and U attachment to those adsorbed HA (i.e., formation of ternary illite-HA-U surface complex). HA adsorbs to clay minerals through association with poly-valent metals (e.g., Al(III)) on clay surface (Greenland, 1971), van der Waals interactions, bridging by aqueous polyvalent metal cations (e.g., Ca^{2+}, Pb^{2+}), and ion/ligand exchange (Liu and Gonzalez, 1999; Arnarson and Keil, 2000). U associates with HA by forming strong inner-sphere U-HA complexes via U binding to hydrophilic functional groups (e.g., carboxylic and phenolic) in HA (Lenhart, et al., 2000; Yang, et al., 2012). U also associates with HA by forming weak U-HA complexes via U binding to hydrophobic (e.g., alkyl and aromatic) carbon in HA (Yang, et al., 2012). The adsorbed HA on clay minerals provides additional binding sites for U, leading to increased U adsorption to clay minerals (Kornilovich, et al., 2000; Krepelova, et al., 2006; Sachs and Bernhard, 2008). In the presence of HA, higher U adsorption to illite at pH 5 compared to pH 9 (87.4% vs. 39.6%) was caused by higher HA adsorption to illite at pH 5. At acidic pH, protonation of functional groups (e.g., carboxyl and phenolic) in HA reduced negative charges on HA, which decreased electrostatic repulsion between HA and clay surface, resulting in higher HA adsorption to clay minerals (Liu and Gonzalez, 1999; Feng, et al., 2005), and consequently higher U attachment to illite. Formation of ternary U surface complexes at acidic pH was previously reported (Lenhart and Honeyman, 1999; Cheng, et al.,

2004).

3.3.3 Illite transport

Fig. 3.1 illustrated the breakthrough curves of illite at pH 5 (Fig. 3.1a) and pH 9 (Fig. 3.1b) and the influecne of HA on illite transport at each pH (C/C_0, C: colloid concentration in the effluent samples; C_0: colloid concentration in the influent; V: total volume of effluent; V_p: pore volume of the packed column). Both pH and HA had strong effects on illite colloids transport: at pH 5, illite breakthrough barely occurred in the U + illite experiments (Fig. 3.1a), indicating nearly all the influent illite colloids were retained in the column. In contrast, at pH 9 high illite breakthrough was observed in the U + illite experiment, and nearly complete breakthrough ($C/C_0 = 0.98 \pm 0.09$) occurred at 6 V_p (Fig. 3.1b). The presence of HA in the influent significantly enhanced illite transport at pH 5: maximum effluent illite concentration (C/C_0) increased from 0 to 1.0 and the overall colloid breakthrough increased from 0 to 72.3 ± 2.0 % (Table 3.2) when HA was present. At pH 9, illite transport increased slightly due to the presence of HA, with the overall colloid recovery increased from 76.2 ± 4.9 % to 87.4 ± 9.8 % when HA was present. At both pH, complete illite breakthrough (i.e., $C/C_0 = 1.0$) occurred in the presence of HA.

Table 3.2: Overall U and illite colloids recovery in the effluent of the column experiments.

pH	Influent	% U Recovery	% Colloid Recovery
5	U	0	NA
	U + illite	0	0
	U + HA	30.5 ±0.0 %	NA
	U + HA + illite	33.7 ±1.0 %	72.3 ±2.0 %
9	U	19.8 ±1.1 %	NA
	U + illite	7.7 ±0.5 %	76.2 ±4.9 %
	U + HA	35.0 ±3.9 %	NA
	U + HA + illite	36.8 ±1.2 %	87.4 ±9.8 %

Colloid deposition is a major process that influences colloid transport in porous media. Colloid deposition rate depends on the overall interactive forces (i.e., van der Waals forces, electric double layer forces, hydration forces, and steric repulsion) between colloid and the media grain (Kretzschmar, et al., 1999). pH influences illite deposition and transport by affecting surface charge of illite colloids and media grains. The dominant minerals (i.e., quartz, albite, and muscovite) in our column were not expected to provide favorable deposition sites for illite colloids because the point of zero charge (pH_{pzc}) of these minerals are low (pH_{pzc} of quartz < 3, albite < 2, muscovite < 4) (Kosmulski, 2011), and therefore these minerals were negatively charged at pH 5 and 9. At both pH 5 and pH 9, illite colloids (pH_{pzc} = 2.5) (Kosmulski, 2011) were also negatively charged (Table 3.1). As such, illite deposition was under unfavorable conditions and high illite transport was expected if illite deposition was only controlled by those minerals. The low illite transport observed at pH 5 in the

absence of HA was the result of illite deposition onto metal (Fe and Al) oxides. In our porous media, concentration of Fe and Al oxides were 718 mg (as Fe) / kg porous media and 211 mg (as Al) / kg porous media respectively (calculated based on the amount of Fe and Al oxides determined by sequential extraction). Although metal oxides is usually a minor component in natural sediments, they substantially influence colloid depostion and transport (Johnson, et al., 1996). While many natural mineral colloids carry negative charges at ambient pH, metal oxides can carry positive charges. The pH_{zpc} for Fe oxides ranges 7.8 ~ 8.5 (Darland and Inskeep, 1997) and for Al oxides ranges 6.5 ~ 7 (Xu, et al., 1991). In our experiments, in the absence of HA, Fe and Al oxides were expected to carry positive charges at pH 5 but negative charges at pH 9. At pH 5, metal oxides in our column provided favorable deposition conditions for negatively charged illite colloids due to strong electrostatic attraction, leading to near complete illite retention in the column. At pH 9, repulsion between the negatively charged metal oxides and illite colloids resulted in near complete illite breakthrough.

Illite transport was enhanced in the presence of HA. At pH 5, maximum illite breakthrough increased from near zero to complete breakthrough when HA was added to the influent (Fig. 3.1a). This drastic increase is attributed to HA adsorption to column materials, especially to Fe and Al oxides. HA adsorbs to metal oxides by electrostatic interactions, association via aliphatic/aromatic carbon, and ligand exchange or H-bonding with carboxyl/ hydroxyl functional groups (Tipping, 1981; Gu, et al., 1994; Fein, et al., 1999; Borggaard, et al., 2005; Yang, et al., 2013). pH controls

the adsorption of HA by influencing the electrostatic interaction between HA and Fe oxides and the number of adsorption sites on Fe oxides (Tipping, 1981; Gu, et al., 1994). In the pH range normally encountered in groundwater, HA carry negative charges due to the dissociation of the acidic groups ($pK_1 = 3.7 \pm 0.1$, $pK_2 = 6.6 \pm 0.1$) (Kretzschmar, et al., 1999; Tombacz, et al., 2000). In our column experiments, at pH 5, negatively charged HA strongly adsorbed to positively charged metal oxides, which diminished or even reversed the positive charges on metal oxides and therefore hindered the deposition of negatively charged illite colloids, leading to increased illite transport. At pH 9, metal oxides were negatively charged, and adsorption of negatively charged HA to metal oxides was weak. Therefore only slight increase in illite transport was observed at pH 9.

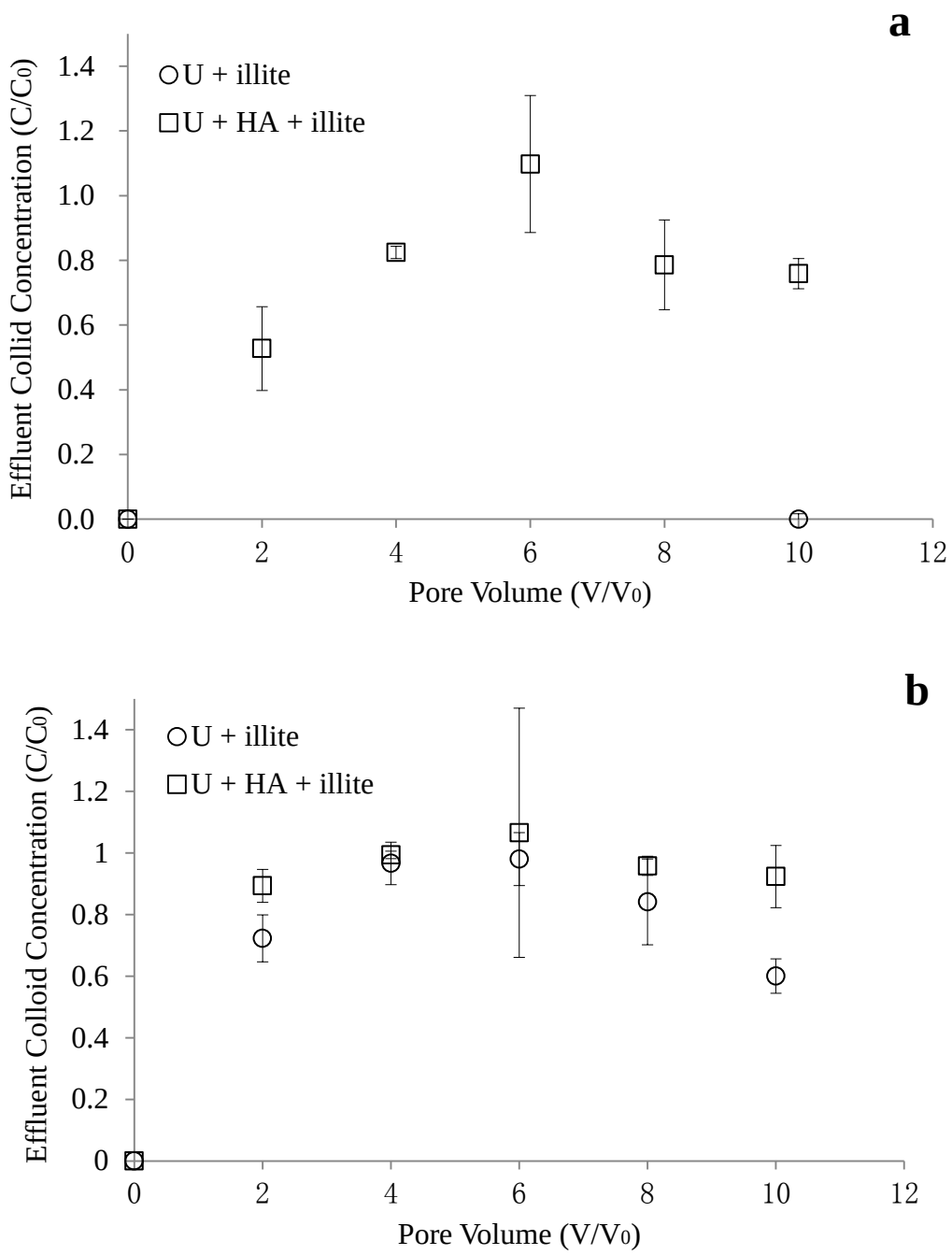

Fig. 3.1: Breakthrough curves of colloids through columns filled with the mixture of till and quartz sand in the absence and presence of HA at pH 5 (a) and pH 9 (b).

Besides metal oxides, HA also adsorbs to clay minerals including illites as discussed in 3.3.2 (Liu and Gonzalez, 1999; Lippold and Lippmann-Pipke, 2009). The association between illite colloids and HA increased negative charges on illite, as

shown by our experimentally measured zeta potential of the illite colloids in the absence and presence of HA (Table 3.1). At both pH 5 and pH 9, zeta potential of illite became more negative due to HA adsorption, which led to increased electrostatics and steric repulsive forces between HA-coated illite and media grain, contributing to higher illite transport (Kretzschmar, et al., 1999; Chen, et al., 2012).

3.3.4 Uranium transport

3.3.4.1 U transport in the absence of HA and illite colloids

U(VI) transport in the absence of HA and illite (U only experiments) was strongly influenced by pH. At pH 5, all the influent U was retained in the column: effluent U concentration was practically zero (Fig. 3.2a: U); at pH 9, U breakthrough was obvious: effluent U concentration increased during the injection of the U-spiked solution, and peaked at 0.26 ± 0.03 at 10 Vp (Fig. 3.2b: U). The overall U recovered in the effluent was 19.8 ± 1.1 % (Table 3.2).

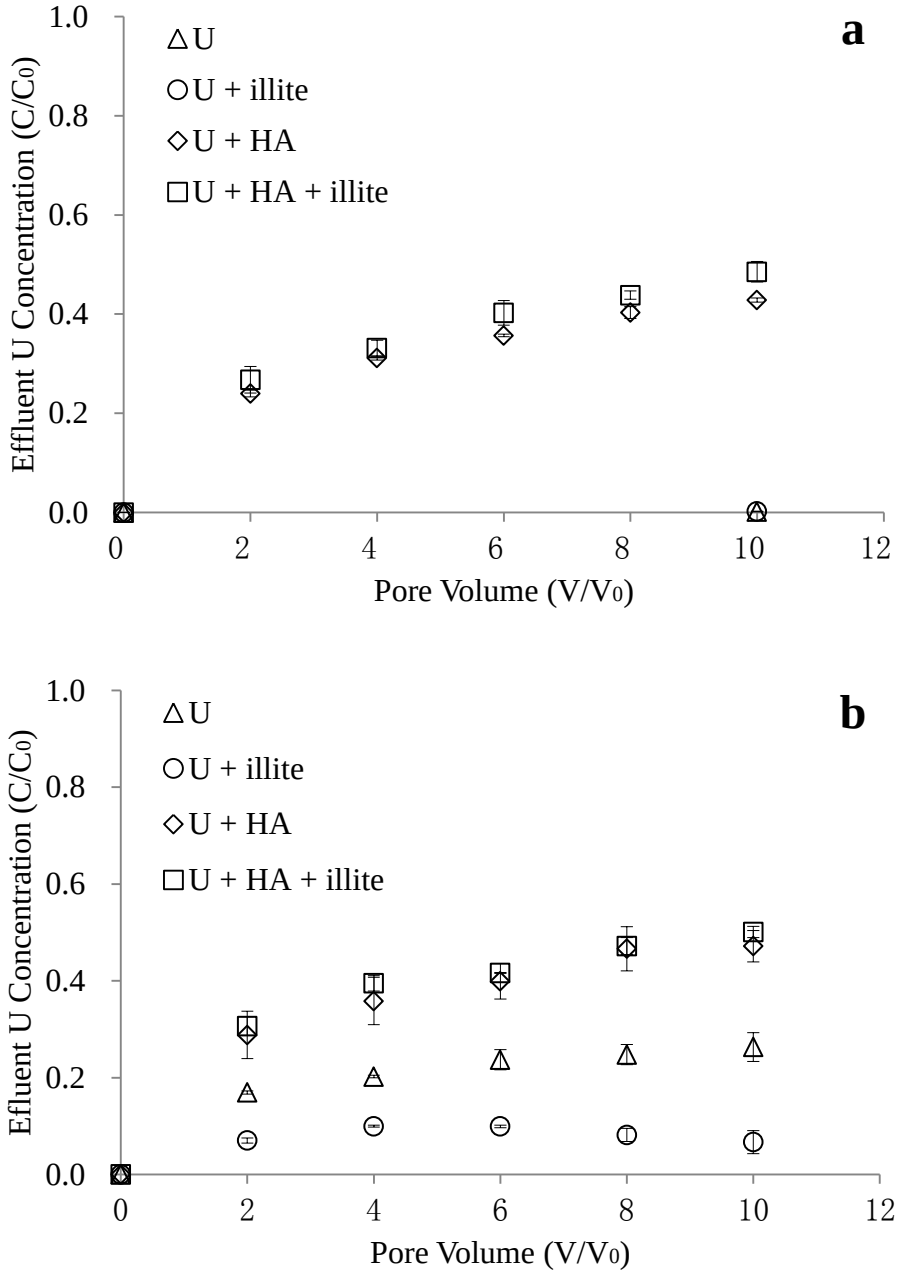

Fig. 3.2: Breakthrough curves of 1 mg/L U(VI) through columns filled with the mixture of till and quartz sand in the absence and presence of HA and illite colloids at pH 5 (a) and pH 9 (b).

In the absence of HA and illite colloids, U transport in porous media is controlled by U adsorption to minerals. All the major mineral constituents (i.e., albite, quartz, and muscovite) in our column material adsorb U (Arnold, et al., 1998; Moyes, et al.,

2000; Prikryl, et al., 2001b). Quartz (Prikryl, et al., 2001b; Fox, et al., 2006) and albite (Walter, et al., 2005) adsorb U through surface complexation, muscovite through surface complexation at aluminol sites on the edge-surface (Arnold, et al., 2006) and surface precipitation on basal plane (Moyes, et al., 2000). The minor component of Fe oxides (718 mg (as Fe) / kg) in column materials also strongly absorbs U. U adsorption to Fe oxides is via formation of inner-sphere surface complexes between UO_2^{2+} (uranyl ion) and Fe oxides (Reich, et al., 1998; Dodge, et al., 2002; Walter, et al., 2003). Arnold et al. (1998) reported that U adsorption to phyllite, a metamorphic rock mainly consists of muscovite, quartz, chlorite and albite, was dominated by U adsorption to the minor component of Fe oxides in the rock in the pH range of 3.5 to 9.5. Barnett et al. (2000) argued that low concentration of Fe oxides (25 g/kg as Fe) in heterogeneous soils dominated U adsorption, based on their observation that soil samples with different physical, chemical, and mineralogical properties but similar Fe oxides content showed very similar pH-dependent U adsorption in the pH range of 2.5 to 10.

U adsorption to minerals is pH dependent. At neutral pH range (i.e., pH = 5.5~7.5), considerable amount of U is adsorbed to albite, quartz, and muscovite; at either low or high pH (pH < 5 or pH > 8), U adsorption is low (Arnold, et al., 1998; Prikryl, et al., 2001b). U adsorption to various Fe oxides such as goethite, hematite, ferrihydrite, and amorphous Fe hydroxide showed similar pH dependence: adsorption increases from near zero at pH 3 to near 100% around pH 5 to 8, then decreases to

near zero at pH > 9 (Hsi and Langmuir, 1985; Waite, et al., 1994; Barnett, et al., 2000; Shuibo, et al., 2009). pH influences U adsorption by controlling mineral surface property and aqueous U species. When pH increases from acidic to near netural, U adsorption increases due to deprotonation of surface sites (Waite, et al., 1994). Additionally, strongly sorbing species such as UO_2^{2+} and $UO_2(OH)^+$ dominate at near netural pH (Prikryl, et al., 2001; Walter, et al., 2005), resulting in high U adsorption. When pH increases further to alkaline range, weakly sorbing U species such as $UO_2(CO_3)_3^{4-}$ and $UO_2(OH_3)^-$ dominate, resulting in low U adsorption (Barnett, et al., 2000; Barnett, et al., 2002). The change in aquesous U species with changing pH and the difference in these aqueous U species' affinity to our major minerals and Fe oxides implies U adsorption is expected to be high at pH 5 but low at pH 9. Therefore, U transport is low at pH 5 but high at pH 9, consistent with our experiemntal observation.

3.3.4.2 Effects of illite colloids

The effects of illite colloids on U transport varied at different pH. At pH 5, no U was detected in our U + illite experiment (Fig. 3.2a), indicating U transport was not enhanced by illite. At pH 9, U was detected in column effluent in our U + illite experiment with an overall effluent U recovery of 7.7 ± 0.5 % (Table 3.2). In spite of apparent U transport in our U + illite experiment at pH 9, U transport was significantly lower compared to that in U only experiment at the same pH with an overall effluent U recovery of 19.8 ± 1.1 %, indicating U transport was hindered by

illite colloids.

The ability of colloids to facilitate contamimant transport depends on the affinity of the colloid for the contaminant and the mobility of the colloid. U adsorption to clay minerals was widely observed (Missana, et al., 2004; Bachmaf and Merkel, 2011). In our U + illite experiments, 19.0 ± 4.9 % of the influent U was associated with illite at pH 5 (Table 3.1). U transport was not enhanced by illite at this pH due to the low mobility of illite (Fig. 3.1a: U+illite). At pH 9, 33.2 ± 4.0 % of the influence U was associated with illite, and illite mobility was high (Fig. 3.1b): at V_p = 2 to 10, effluent illite concentration > 0.6. Therefore, it was expected that illite colloid would increase U transport. However, effluent U concentration in our U + illite experiment was even lower than that in U only experiment (Fig. 3.2b). This surprising low U transport is worth further discussion. Although illite transport was quite high at pH 9 in our U + illite experiment, a significant portion (100% - 76.2% = 23.8%) of the injected illite was retained in the column (Table 3.2). The retention of those illite colloids also immobilized the U associated with them, reducing U transport. However, this process alone cannot fully explain the low U transport observed in our U + illite experiment, since this process can only immobolize 23.8% of the illite-associated U in the influent, i.e., 23.8% × 33.2% ≈ 7.9% of the total U in the influent, which was much lower than the experimentally measured U immobolization (100% - 7.7% = 92.3%). The additional U immobilization was attributed to adsorption of aqueous U to column materials (66.8% of influent U was in aqueous phase), and U desorption from illite

during illite transport through the column. In the influent (U-spiked illite suspension), aqueous U and illite-associated U were at adsorption equilibrium, and the ratio of illite-associatd U concentration to aqueous U concentration was constrained by U distribution coefficient. When the U-spiked illite suspension was injected into the column, aqueous U concentration decreased due to its adsorption to major minerals (quartz, albite, and muscovite) and Fe oxides. The decrease in aqueous U concentration induced U desorption from illite. The extent of desorption depends on the equilibrium and kinetics of desorption and adsorption reactions. The higher affinity of column materials for U, and the faster U desorbs and adsorbs, the greater amount of U will desorb. The substantial desorption observed in our experiments demonstrates the column materials had high affinity for U, and that both U desorption and adsorption were fast. In addition, this result shows the ability of colloid to facilitate contaminant transport is influenced by competition for contaminants between colloid and aquifer minerals. The presence of strongly sorbing minerals (e.g., Fe oxides) could render the colloids an ineffective "shield" for contaminant transport.

3.3.4.3 Effects of HA

In the presence of HA, U transport was accelerated and the maximum U breakthrough increased. At pH 5, U breakthrough occurred soon after the injection of U-spiked influent. Compared to the near zero U breakthrough in U only experiment, overall effluent U recovery reached 30.5 ± 0.0 % in the U + HA experiment (Table 3.2). At pH 9, elevated U breakthrough was observed as well, with the overall effluent

U recovery increased from 19.8 ± 1.1 % (U only experiment) to 35.0 ± 3.9 % (U + HA experiment).

Enhanced U transport by HA has been reported (Sachs, et al., 2006; Mibus, et al., 2007; Yang, et al., 2012). One mechanism for the increased U transport in the presence of HA is association of aqueous U with aqueous HA. Aqueous U can form U-HA complexes via reacting with hydrophilic functional groups in HA (carboxylic and phenolic) (Lenhart, et al., 2000; Yang, et al., 2012) as well as with hydrophobic (alkyl and aromatic) carbon (Yang, et al., 2012). The formation of aqueous U-HA complexes "shielded" U from adsorption to column materials and increased U transport. The other mechanism for increased U transport in the presence of HA is competition between HA and aqueous U for surface sites on column materials, which made U less adsorbing and more mobile. As discussed in 3.3.3, negatively charged HA adsorbs to metal oxides (Tipping, 1981; Gu, et al., 1994; Yang, et al., 2013). HA also adsorbes to the main minerals in our column (i.e. albite, quartz, and muscovite) (Schmeide, et al., 2000; Pitois, et al., 2008).

U breakthrough at pH 9 in our U + HA experiment was slightly higher than that at pH 5 (Fig. 3.2) (overall effluent U recovery = 35.0 ± 3.9 % at pH 9 vs. 30.5 ± 0.0 % at pH 5). This was due to higher HA mobility and higher U binding strength of HA at high pH. At pH 5, negatively charged HA (pK_1=3.7 ± 0.1, pK_2=6.6 ± 0.1, (Tombacz, et al., 2000)) adsorption to the positively charged Fe oxides (pH_{pzc} 7.8 ~ 8.5, (Darland and Inskeep, 1997)) and main minerals (pH_{pzc} of quartz < 3, albite < 2, muscovite < 4,

(Kosmulski, 2011)) was relatively strong; at pH 9, metal oxides became negatively charged and main minerals and HA became more negatively charged, resulting in less HA adsorption and higher mobility of HA. Additionally, the binding of U by HA is stronger at higher pH (Li, et al., 1980; Lenhart, et al., 2000), which also contributed to higher mobility of HA-associated U at pH 9.

3.3.4.4 U transport in the presence of HA and illite colloids

At both pH 5 and 9, U breakthrough was the highest in U + HA + illite experiments (Fig. 3.2). The overall effluent U recovery in the U + HA + illite experiments reached 33.7 ± 1.0 % (pH 5) and 36.8 ± 1.2 % (pH 9) (Table 3.2). Effluent U concentration in the U + HA + illite experiments from 2 Vp to 10 Vp was slightly higher compared to that in the U + HA experiments at either pH 5 or 9 (t-test, $p < 0.05$), and was much higher than those in U only and U + illite experiments.

In the presence of both HA and illite, the high transport of U was primary due to HA-facilitated U transport. The higher U breakthrough in U + HA + illite experiments compared to U + HA experiments indicated that illite further enhanced U transport. The ability of illite to promote U transport depends on the mobility of illite and the affinity of illite to U. As discussed in 3.3.3, in the presence of HA, the mobility of illite was greatly enhanced due to HA adsorption to column materials and to illite, especially at pH 5 (Fig. 3.1). As discussed in 3.3.2, formation of ternary illite-HA-U surface complexes substantially increased U adsorption to illite, especially at pH 5 (Table 3.1). Therefore, illite-associated U made additional contribution to U transport

in the U + HA + illite experiments, resulting in higher U transport compared to that in U + HA experiments. The extent of increase in illite transport and U adsorption to illite due to the presence of HA was much lower at pH 9 than that at pH 5 (Fig. 3.2 and Table 3.1), therefore, at pH 9 only slight increase in U transport (relative to that in U + HA experiments) was observed.

3.4 Conclusions and Implications

Both illite colloids and HA influences U transport via a suite of interfacial and aqueous geochemical reactions that include: (i) HA adsorption to illite colloids and geologic media, (ii) U adsorption to illite colloids and geologic media, (iii) formation of aqueous HA-U complexes, and (iv) formation of ternary colloid-HA-U surface complexes. Illite colloids had no observable influence on U transport at low pH due to its low mobility. At high pH, illite decreased U transport due to U desorption from illite. HA not only increased illite colloid transport, but also increased U transport via competition with U for adsorptive sites on geologic materials and formation of aqueous U-HA complexes. When both illite colloids and HA were present, formation of ternary illite-HA-U surface complexes and HA adsorption to geologic media and illite colloids enhanced both U and illite transport. Natural organic matter (e.g., HA) plays a significant and complicated role in mediating U transport both in the absence and presence of mineral colloids. The ubiquitous co-existence of mineral colloids (e.g., illite) and natural organic matter (e.g., HA) in subsurface environment implies that the combined effects of mineral colloids and natural organic matter must be considered

when estimating U transport in real subsurface environments.

3.5 References

Antelo, J., Arce, F., Avena, M., Fiol, S., Lopez, R., and Macias, F. (2007). Adsorption of a soil humic acid at the surface of goethite and its competitive interaction with phosphate. *Geoderma, 138*(1-2), 12-19.

Arnarson, T. S., and Keil, R. G. (2000). Mechanisms of pore water organic matter adsorption to montmorillonite. *Marine Chemistry, 71*(3–4), 309-320.

Arnold, T., Utsunomiya, S., Geipel, G., Ewing, R. C., Baumann, N., and Brendler, V. (2006). Adsorbed U(VI) Surface Species on Muscovite Identified by Laser Fluorescence Spectroscopy and Transmission Electron Microscopy. *Environmental Science & Technology, 40*(15), 4646-4652.

Arnold, T., Zorn, T., Bernhard, G., and Nitsche, H. (1998). Sorption of uranium(VI) onto phyllite. *Chemical Geology, 151*(1–4), 129-141.

Artinger, R., Rabung, T., Kim, J. I., Sachs, S., Schmeide, K., Heise, K. H., Bernhard, G., and Nitsche, H. (2002). Humic colloid-borne migration of uranium in sand columns. *Journal of Contaminant Hydrology, 58*(1–2), 1-12.

Babu, M., Somashekar, R., Kumar, S., Shivanna, K., Krishnamurthy, V., and Eappen, K. (2008). Concentration of uranium levels in groundwater. *International Journal of Environmental Science and Technology, 5*(2), 263-266.

Bachmaf, S., and Merkel, B. J. (2011). Sorption of uranium(VI) at the clay mineral-water interface. *Environmental Earth Sciences, 63*(5), 925-934.

Baek, I., and Pitt, W. W. (1996). Colloid-facilitated radionuclide transport in fractured porous rock. *Waste Management, 16*(4), 313-325.

Barnett, M. O., Jardine, P. M., and Brooks, S. C. (2002). U(VI) adsorption to heterogeneous subsurface media: Application of a surface complexation model. *Environmental Science & Technology, 36*(5), 937-942.

Barnett, M. O., Jardine, P. M., Brooks, S. C., and Selim, H. M. (2000). Adsorption and transport of uranium(VI) in subsurface media. *Soil Science Society of America Journal, 64*(3), 908-917.

Bekhit, H. M., and Hassan, A. E. (2007). Subsurface contaminant transport in the presence of colloids: Effect of nonlinear and nonequilibrium interactions. *Water Resources Research, 43*(8).

Borggaard, O. K., Raben-Lange, B., Gimsing, A. L., and Strobel, B. W. (2005). Influence of humic substances on phosphate adsorption by aluminium and iron oxides. *Geoderma, 127*(3–4), 270-279.

Chau, N. D., Dulinski, M., Jodlowski, P., Nowak, J., Rozanski, K., Sleziak, M., and Wachniew, P. (2011). Natural radioactivity in groundwater - a review. *Isotopes in Environmental and Health Studies, 47*(4), 415-437.

Chen, G. X., Liu, X. Y., and Su, C. M. (2012). Distinct Effects of Humic Acid on Transport and Retention of TiO2 Rutile Nanoparticles in Saturated Sand Columns. *Environmental Science & Technology, 46*(13), 7142-7150.

Cheng, T., Barnett, M. O., Roden, E. E., and Zhuang, J. L. (2004). Effects of phosphate on uranium(VI) adsorption to goethite-coated sand. *Environmental Science & Technology, 38*(22), 6059-6065.

Cheng, T., Barnett, M. O., Roden, E. E., and Zhunag, J. L. (2007). Reactive transport of uranium(VI) and phosphate in a goethite-coated sand column: An experimental study. *Chemosphere, 68*(7), 1218-1223.

Chisholm-Brause, C. J., Berg, J. M., Little, K. M., Matzner, R. A., and Morris, D. E. (2004). Uranyl sorption by smectites: spectroscopic assessment of thermodynamic modeling. *Journal of Colloid and Interface Science, 277*(2), 366-382.

Crancon, P., Pili, E., and Charlet, L. (2010). Uranium facilitated transport by water-dispersible colloids in field and soil columns. *Science of the Total Environment, 408*(9), 2118-2128.

Darland, J. E., and Inskeep, W. P. (1997). Effects of pH and phosphate competition on the transport of arsenate. *Journal of Environmental Quality, 26*(4), 1133-1139.

Datta, A., Sanyal, S. K., and Saha, S. (2001). A study on natural and synthetic humic acids and their complexing ability towards cadmium. *Plant and Soil, 235*(1), 115-125.

Dodge, C. J., Francis, A. J., Gillow, J. B., Halada, G. P., Eng, C., and Clayton, C. R. (2002). Association of Uranium with Iron Oxides Typically Formed on Corroding Steel Surfaces. *Environmental Science & Technology, 36*(16), 3504-3511.

Dresel, P. E., Wellman, D. M., Cantrell, K. J., and Truex, M. J. (2011). Review: Technical and Policy Challenges in Deep Vadose Zone Remediation of Metals

and Radionuclides. *Environmental Science & Technology, 45*(10), 4207-4216.

Fein, J. B., Boily, J.-F., Güçlü, K., and Kaulbach, E. (1999). Experimental study of humic acid adsorption onto bacteria and Al-oxide mineral surfaces. *Chemical Geology, 162*(1), 33-45.

Feng, X., Simpson, A. J., and Simpson, M. J. (2005). Chemical and mineralogical controls on humic acid sorption to clay mineral surfaces. *Organic Geochemistry, 36*(11), 1553-1566.

Fox, P. M., Davis, J. A., and Zachara, J. M. (2006). The effect of calcium on aqueous uranium(VI) speciation and adsorption to ferrihydrite and quartz. *Geochimica Et Cosmochimica Acta, 70*(6), 1379-1387.

Gabriel, U., Gaudet, J. P., Spadini, L., and Charlet, L. (1998). Reactive transport of uranyl in a goethite column: an experimental and modelling study. *Chemical Geology, 151*(1-4), 107-128.

Giasuddin, A. B. M., Kanel, S. R., and Choi, H. (2007). Adsorption of humic acid onto nanoscale zerovalent iron and its effect on arsenic removal. *Environmental Science & Technology, 41*(6), 2022-2027.

Gradusov, B. P. (1974). A tentative study of clay mineral distribution in soils of the world. *Geoderma, 12*(1–2), 49-55.

Greenland, D. J. (1971). Interactions between humic and fulvic acids and clays. *Soil Science, 111*(1), 34-&.

Grolimund, D., Borkovec, M., Barmettler, K., and Sticher, H. (1996).

Colloid-facilitated transport of strongly sorbing contaminants in natural porous media: A laboratory column study. *Environmental Science & Technology, 30*(10), 3118-3123.

Gu, B. H., Schmitt, J., Chen, Z. H., Liang, L. Y., and McCarthy, J. F. (1994). Adsorption and desorption of natural organic matter on iron-oxide: mechanisms and models. *Environmental Science & Technology, 28*(1), 38-46.

Hsi, C. K. D., and Langmuir, D. (1985). Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochimica Et Cosmochimica Acta, 49*(9), 1931-1941.

Jerden Jr, J. L., and Sinha, A. K. (2006). Geochemical coupling of uranium and phosphorous in soils overlying an unmined uranium deposit: Coles Hill, Virginia. *Journal of Geochemical Exploration, 91*(1–3), 56-70.

Johnson, P. R., Sun, N., and Elimelech, M. (1996). Colloid transport in geochemically heterogeneous porous media: Modeling and measurements. *Environmental Science & Technology, 30*(11), 3284-3293.

Kalbitz, K., and Wennrich, R. (1998). Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *Science of the Total Environment, 209*(1), 27-39.

Kaplan, D. I., Bertsch, P. M., Adriano, D. C., and Orlandini, K. A. (1994). Actinide association with groundwater colloids in a coastal-plain aquifer. *Radiochimica Acta, 66-7*, 181-187.

Kim, J. I., Delakowitz, B., Zeh, P., Klotz, D., and Lazik, D. (1994). A column experiment for the study of colloidal radionuclide migration in Gorleben aquifer systems. *Radiochimica Acta, 66-7*, 165-171.

Kornilovich, B., Pshinko, G., Spasenova, L., and Kovalchuk, I. (2000). Influence of humic substances on the sorption interactions between lanthanide and actinide ions and clay minerals. *Adsorption Science & Technology, 18*(10), 873-880.

Kosmulski, M. (2011). The pH-dependent surface charging and points of zero charge: V. Update. *Journal of Colloid and Interface Science, 353*(1), 1-15.

Kostic, I., Andelkovic, T., Nikolic, R., Bojic, A., Purenovic, M., Blagojevic, S., and Andelkovic, D. (2011). Copper(II) and lead(II) complexation by humic acid and humic-like ligands. *Journal of the Serbian Chemical Society, 76*(9), 1325-1336.

Krepelova, A., Sachs, S., and Bernhard, G. (2006). Uranium(VI) sorption onto kaolinite in the presence and absence of humic acid. *Radiochimica Acta, 94*(12), 825-833.

Kretzschmar, R., Borkovec, M., Grolimund, D., and Elimelech, M. (1999). Mobile subsurface colloids and their role in contaminant transport. *Advances in Agronomy, Vol 66, 66*, 121-193.

Kretzschmar, R., and Schafer, T. (2005). Metal retention and transport on colloidal particles in the environment. *Elements, 1*(4), 205.

Kronfeld, J., Godfrey-Smith, D. I., Johannessen, D., and Zentilli, M. (2004). Uranium

series isotopes in the Avon Valley, Nova Scotia. *Journal of Environmental Radioactivity, 73*(3), 335-352.

Lenhart, J. J., Cabaniss, S. E., MacCarthy, P., and Honeyman, B. D. (2000). Uranium (VI) complexation with citric, humic and fulvic acids. *Radiochimica Acta, 88*(6/2000), 345.

Lenhart, J. J., and Honeyman, B. D. (1999). Uranium(VI) sorption to hematite in the presence of humic acid. *Geochimica Et Cosmochimica Acta, 63*(19–20), 2891-2901.

Li, W. C., Victor, D. M., and Chakrabarti, C. L. (1980). Effect of pH and uranium concentration on interaction of uranium (VI) and uranium (IV) with organic ligands in aqueous solutions. *Analytical chemistry, 52*(3), 520-523.

Lienert, C., Short, S. A., and Vongunten, H. R. (1994). Uranium infiltration from a river to shallow groundwater. *Geochimica Et Cosmochimica Acta, 58*(24), 5455-5463.

Lippold, H., and Lippmann-Pipke, J. (2009). Effect of humic matter on metal adsorption onto clay materials: Testing the linear additive model. *Journal of Contaminant Hydrology, 109*(1–4), 40-48.

Liu, A. G., and Gonzalez, R. D. (1999). Adsorption/desorption in a system consisting of humic acid, heavy metals, and clay minerals. *Journal of Colloid and Interface Science, 218*(1), 225-232.

McKinley, J. P., Zachara, J. M., Smith, S. C., and Turner, G. D. (1995). The influence

of uranyl hydrolysis and multiple site-binding reactions on adsorption of U(VI) to montmorillonite. *Clays and Clay Minerals, 43*(5), 586-598.

Metreveli, G., Abbt-Braun, G., and Frimmel, F. H. (2010). Influence of NOM on the Mobility of Metal(loid)s in Water-Saturated Porous Media. *Aquatic Geochemistry, 16*(1), 85-100.

Mibus, J., Sachs, S., Pfingsten, W., Nebelung, C., and Bernhard, G. (2007). Migration of uranium(IV)/(VI) in the presence of humic acids in quartz sand: A laboratory column study. *Journal of Contaminant Hydrology, 89*(3-4), 199-217.

Missana, T., Garcia-Gutierrez, M., and Alonso, U. (2004). Kinetics and irreversibility of cesium and uranium sorption onto bentonite colloids in a deep granitic environment. *Applied Clay Science, 26*(1-4), 137-150.

Morales, V. L., Zhang, W., Gao, B., Lion, L. W., Bisogni, J. J., McDonough, B. A., and Steenhuis, T. S. (2011). Impact of dissolved organic matter on colloid transport in the vadose zone: Deterministic approximation of transport deposition coefficients from polymeric coating characteristics. *Water Research, 45*(4), 1691-1701.

Moyes, L. N., Parkman, R. H., Charnock, J. M., Vaughan, D. J., Livens, F. R., Hughes, C. R., and Braithwaite, A. (2000). Uranium Uptake from Aqueous Solution by Interaction with Goethite, Lepidocrocite, Muscovite, and Mackinawite: An X-ray Absorption Spectroscopy Study. *Environmental Science & Technology,*

34(6), 1062-1068.

Pitois, A., Abrahamsen, L. G., Ivanov, P. I., and Bryan, N. D. (2008). Humic acid sorption onto a quartz sand surface: A kinetic study and insight into fractionation. *Journal of Colloid and Interface Science, 325*(1), 93-100.

Prikryl, J. D., Jain, A., Turner, D. R., and Pabalan, R. T. (2001). UraniumVI sorption behavior on silicate mineral mixtures. *Journal of Contaminant Hydrology, 47*(2–4), 241-253.

Ransom, B., and Helgeson, H. C. (1993). Compositional end members and thremodynamic components of illite and dioctahedral aluminous smectite solid-solutions. *Clays and Clay Minerals, 41*(5), 537-550.

Reich, T., Moll, H., Arnold, T., Denecke, M. A., Hennig, C., Geipel, G., Bernhard, G., Nitsche, H., Allen, P. G., Bucher, J. J., Edelstein, N. M., and Shuh, D. K. (1998). An EXAFS study of uranium(VI) sorption onto silica gel and ferrihydrite. *Journal of Electron Spectroscopy and Related Phenomena, 96*(1–3), 237-243.

Sachs, S., and Bernhard, G. (2008). Sorption of U(VI) onto an artificial humic substance-kaolinite-associate. *Chemosphere, 72*(10), 1441-1447.

Sachs, S., Geipel, G., Mibus, J., and Bernhard, G. (2006). Impact of humic acid on the uranium migration in the environment

Uranium in the Environment. In B. J. Merkel & A. Hasche-Berger (Eds.), (pp. 107-116): Springer Berlin Heidelberg.

Saiers, J. E., and Hornberger, G. M. (1999). The influence of ionic strength on the facilitated transport of cesium by kaolinite colloids. *Water Resources Research, 35*(6), 1713-1727.

Schmeide, K., Pompe, S., Bubner, M., Heise, K. H., Bernhard, G., and Nitsche, H. (2000). Uranium(VI) sorption onto phyllite and selected minerals in the presence of humic acid. *Radiochimica Acta, 88*(9-11), 723-728.

Schmitt, D., Saravia, F., Frimmel, F. H., and Schuessler, W. (2003). NOM-facilitated transport of metal ions in aquifers: importance of complex-dissociation kinetics and colloid formation. *Water Research, 37*(15), 3541-3550.

Shuibo, X., Chun, Z., Xinghuo, Z., Jing, Y., Xiaojian, Z., and Jingsong, W. (2009). Removal of uranium (VI) from aqueous solution by adsorption of hematite. *Journal of Environmental Radioactivity, 100*(2), 162-166.

Tessier, A., Campbell, P. G., and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical chemistry, 51*(7), 844-851.

Tipping, E. (1981). The adsorption of aquatic humic substances by iron oxides. *Geochimica Et Cosmochimica Acta, 45*(2), 191-199.

Tombacz, E., Dobos, A., Szekeres, M., Narres, H. D., Klumpp, E., and Dekany, I. (2000). Effect of pH and ionic strength on the interaction of humic acid with aluminium oxide. *Colloid and Polymer Science, 278*(4), 337-345.

Waite, T. D., Davis, J. A., Payne, T. E., Waychunas, G. A., and Xu, N. (1994).

Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. *Geochimica Et Cosmochimica Acta, 58*(24), 5465-5478.

Walter, M., Arnold, T., Geipel, G., Scheinost, A., and Bernhard, G. (2005). An EXAFS and TRLFS investigation on uranium(VI) sorption to pristine and leached albite surfaces. *Journal of Colloid and Interface Science, 282*(2), 293-305.

Walter, M., Arnold, T., Reich, T., and Bernhard, G. (2003). Sorption of Uranium(VI) onto Ferric Oxides in Sulfate-Rich Acid Waters. *Environmental Science & Technology, 37*(13), 2898-2904.

Wang, T., Liu, W., Xiong, L., Xu, N., and Ni, J. R. (2013). Influence of pH, ionic strength and humic acid on competitive adsorption of Pb(II), Cd(II) and Cr(III) onto titanate nanotubes. *Chemical Engineering Journal, 215*, 366-374.

Xu, H., Allard, B., and Grimvall, A. (1991). Effects of acidification and natural organic materials on the mobility of arsenic in the environment. *Water Air and Soil Pollution, 57-8*, 269-278.

Yang, Y., Saiers, J. E., and Barnett, M. O. (2013). Impact of Interactions between Natural Organic Matter and Metal Oxides on the Desorption Kinetics of Uranium from Heterogeneous Colloidal Suspensions. *Environmental Science & Technology, 47*(6), 2661-2669.

Yang, Y., Saiers, J. E., Xu, N., Minasian, S. G., Tyliszczak, T., Kozimor, S. A., Shuh, D. K., and Barnett, M. O. (2012). Impact of Natural Organic Matter on Uranium Transport through Saturated Geologic Materials: From Molecular to

Column Scale. *Environmental Science & Technology, 46*(11), 5931-5938.

Yoshida, T., and Suzuki, M. (2008). Effects of humic acid on migration of montmorillonite and alumina colloid in a quartz sand column. *Colloids and Surfaces a-Physicochemical and Engineering Aspects, 325*(3), 115-119.

Chapter 4. Summary and Conclusions

Natural organic matter (NOM) and mineral colloids, which are ubiquitous in groundwater and the vadose zone, could strongly influence contaminant transport in subsurface environment. Arsenic (As) and uranium (U) are common contaminants in groundwater threatening human health. To accurately assess As and U migration in groundwater, knowledge of the influence of NOM and mineral colloids on As and U transport is essential. This thesis research investigated the interactions between NOM, mineral colloids, and As or U under ambient conditions, and elucidated the effects of NOM and mineral colloids on As and U transport in porous geo-media.

To ascertain the influence of NOM and mineral colloids on As transport, column experiments were conducted by injecting As-spiked solution/suspension into vertically oriented glass columns packed with mixed natural sediments and pure quartz sand, and collecting and analyzing As concentration in column effluent (Chapter 2). Humic acid (HA), which is a major component of NOM, was used as a proxy for NOM. Illite was used as a representative mineral colloid due to its abundance in natural subsurface environment. Eight column experiments, distinguished based on the composition of the As-containing solution/suspension (As only, As + illite, As + HA, and As + illite + HA) and solution pH (pH 5 and pH 9), were performed. Results showed that illite colloids had minor influence on As transport at pH 5 due to the low mobility of illite colloids, but they decreased As transport at pH 9 due to As desorption from illite colloids. HA enhanced As transport at both pH 5 and pH 9 via competition with As for

adsorptive sites on column materials and formation of aqueous As-HA complexes. When illite colloids and HA co-existed, high illite breakthrough occurred. As transport was enhanced compared to that in As only and As + illite systems, but lower than that in As + HA system due to HA adsorption to illite colloids, which effectively decreased aqueous phase HA concentration and hindered HA-enhanced As transport.

Using a similar method, I investigated the influence of NOM and mineral colloids on U transport in water saturated geological materials under different water chemistry conditions (Chapter 3). Humic acid (HA) and illite were used as proxies of NOM and mineral colloids respectively. U and colloid transport was investigated by injecting U-containing solution/suspension into water-saturated columns packed with well mixed natural sediment and quartz sand, and analyzing U and illite concentration in column effluent. Eight column experiments, distinguished by influent composition (U only, U + illite, U + HA, and U + illite + HA) and pH (5 and 9), were performed. Results showed that U transport was pH-dependent, and mineral colloids and HA influenced U transport in different manners. Illite colloids had minor effects on U transport at pH 5 due to the low mobility of illite colloids. At pH 9, overall illite breakthrough increased to due to high repulsive forces between illite colloids and column materials, but U transport decreased due to desorption of U from illite. HA increased U breakthrough at both pH 5 and pH 9 via (i) competition with U for adsorptive sites on geologic materials and (ii) formation of aqueous U-HA complexes. In the presence of both illite colloids and HA, formation of ternary illite-HA-U surface

complexes and HA adsorption to geologic media and illite colloids increased both U and illite transport. Since NOM and mineral colloids usually co-exist in natural subsurface environment, it is necessary to consider the combined effects of NOM and mineral colloids when assessing U transport in groundwater and the vadose zone.

Works Cited

Abbasnejad, A., Mirzaie, A., Derakhshani, R., and Esmaeilzadeh, E. (2013). Arsenic in groundwaters of the alluvial aquifer of Bardsir plain, SE Iran. *Environmental Earth Sciences, 69*(8), 2549-2557.

Ahmed, K. M., Bhattacharya, P., Hasan, M. A., Akhter, S. H., Alam, S. M. M., Bhuyian, M. A. H., Imam, M. B., Khan, A. A., and Sracek, O. (2004). Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. *Applied Geochemistry, 19*(2), 181-200.

Aiuppa, A., Avino, R., Brusca, L., Caliro, S., Chiodini, G., D'Alessandro, W., Favara, R., Federico, C., Ginevra, W., Inguaggiato, S., Longo, M., Pecoraino, G., and Valenza, M. (2006). Mineral control of arsenic content in thermal waters from volcano-hosted hydrothermal systems: Insights from island of Ischia and Phlegrean Fields (Campanian Volcanic Province, Italy). *Chemical Geology, 229*(4), 313-330.

Akbour, R. A., Douch, J., Hamdani, M., and Schmitz, P. (2002). Transport of kaolinite colloids through quartz sand: Influence of humic acid, Ca2+, and trace metals. *Journal of Colloid and Interface Science, 253*(1), 1-8.

Akter, A., and Ali, M. H. (2011). Arsenic contamination in groundwater and its proposed remedial measures. *International Journal of Environmental Science and Technology, 8*(2), 433-443.

Ames, L. L., McGarrah, J. E., and Walker, B. A. (1983). Sorption of Uranium and

Radium by Biotite, Muscovite, and Phlogopite. *Clays and Clay Minerals, 31*(5), 343-351.

Andersson, P. S., Porcelli, D., Gustafsson, Ö., Ingri, J., and Wasserburg, G. J. (2001). The importance of colloids for the behavior of uranium isotopes in the low-salinity zone of a stable estuary. *Geochimica Et Cosmochimica Acta, 65*(1), 13-25.

Antelo, J., Arce, F., Avena, M., Fiol, S., Lopez, R., and Macias, F. (2007). Adsorption of a soil humic acid at the surface of goethite and its competitive interaction with phosphate. *Geoderma, 138*(1-2), 12-19.

Antelo, J., Avena, M., Fiol, S., Lopez, R., and Arce, F. (2005). Effects of pH and ionic strength on the adsorption of phosphate and arsenate at the goethite-water interface. *Journal of Colloid and Interface Science, 285*(2), 476-486.

Arnarson, T. S., and Keil, R. G. (2000). Mechanisms of pore water organic matter adsorption to montmorillonite. *Marine Chemistry, 71*(3–4), 309-320.

Arnold, T., Utsunomiya, S., Geipel, G., Ewing, R. C., Baumann, N., and Brendler, V. (2006). Adsorbed U(VI) Surface Species on Muscovite Identified by Laser Fluorescence Spectroscopy and Transmission Electron Microscopy. *Environmental Science & Technology, 40*(15), 4646-4652.

Arnold, T., Zorn, T., Bernhard, G., and Nitsche, H. (1998). Sorption of uranium(VI) onto phyllite. *Chemical Geology, 151*(1–4), 129-141.

Artinger, R., Rabung, T., Kim, J. I., Sachs, S., Schmeide, K., Heise, K. H., Bernhard,

G., and Nitsche, H. (2002). Humic colloid-borne migration of uranium in sand columns. *Journal of Contaminant Hydrology, 58*(1–2), 1-12.

Babu, M., Somashekar, R., Kumar, S., Shivanna, K., Krishnamurthy, V., and Eappen, K. (2008). Concentration of uranium levels in groundwater. *International Journal of Environmental Science and Technology, 5*(2), 263-266.

Bachmaf, S., and Merkel, B. J. (2011). Sorption of uranium(VI) at the clay mineral-water interface. *Environmental Earth Sciences, 63*(5), 925-934.

Baek, I., and Pitt, W. W. (1996). Colloid-facilitated radionuclide transport in fractured porous rock. *Waste Management, 16*(4), 313-325.

Bargar, J. R., Reitmeyer, R., and Davis, J. A. (1999). Spectroscopic confirmation of uranium(VI)-carbonato adsorption complexes on hematite. *Environmental Science & Technology, 33*(14), 2481-2484.

Barnett, M. O., Jardine, P. M., and Brooks, S. C. (2002). U(VI) adsorption to heterogeneous subsurface media: Application of a surface complexation model. *Environmental Science & Technology, 36*(5), 937-942.

Barnett, M. O., Jardine, P. M., Brooks, S. C., and Selim, H. M. (2000). Adsorption and transport of uranium(VI) in subsurface media. *Soil Science Society of America Journal, 64*(3), 908-917.

Bauer, M., and Blodau, C. (2006). Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. *Science of the Total Environment, 354*(2-3), 179-190.

Baumann, T., Fruhstorfer, P., Klein, T., and Niessner, R. (2006). Colloid and heavy metal transport at landfill sites in direct contact with groundwater. *Water Research, 40*(14), 2776-2786.

Bekhit, H. M., and Hassan, A. E. (2007). Subsurface contaminant transport in the presence of colloids: Effect of nonlinear and nonequilibrium interactions. *Water Resources Research, 43*(8).

Betcher, R. N., Gascoyne, M., and Brown, D. (1988). Uranium in groundwater of southeastern Manitoba, Canada. *Canadian Journal of Earth Sciences, 25*(12), 2089-2103.

Borggaard, O. K., Raben-Lange, B., Gimsing, A. L., and Strobel, B. W. (2005). Influence of humic substances on phosphate adsorption by aluminium and iron oxides. *Geoderma, 127*(3–4), 270-279.

Boyle, D. R., Turner, R. J. W., and Hall, G. E. M. (1998). Anomalous arsenic concentrations in groundwaters of an island community, Bowen Island, British Columbia. *Environmental Geochemistry and Health, 20*(4), 199-212.

Buschmann, J., Kappeler, A., Lindauer, U., Kistler, D., Berg, M., and Sigg, L. (2006). Arsenite and arsenate binding to dissolved humic acids: Influence of pH, type of humic acid, and aluminum. *Environmental Science & Technology, 40*(19), 6015-6020.

Campos, B., Aguilar-Carrillo, J., Algarra, M., Gonçalves, M. A., Rodríguez-Castellón, E., Esteves da Silva, J. C. G., and Bobos, I. (2013). Adsorption of uranyl ions

on kaolinite, montmorillonite, humic acid and composite clay material. *Applied Clay Science, 85*(0), 53-63.

Celine, C. L., Lespes, G., Dubascoux, S., Aupiais, J., Pointurier, F., and Potin-Gautier, M. (2009). Colloidal transport of uranium in soil: Size fractionation and characterization by field-flow fractionation-multi-detection. *Journal of Chromatography A, 1216*(52), 9113-9119.

Chakraborty, S., Wolthers, M., Chatterjee, D., and Charlet, L. (2007). Adsorption of arsenite and arsenate onto muscovite and biotite mica. *Journal of Colloid and Interface Science, 309*(2), 392-401.

Charlet, L., Chakraborty, S., Varma, S., Tournassat, C., Wolthers, M., Chatterjee, D., and Ross, G. R. (2005). Adsorption and heterogeneous reduction of arsenic at the phyllosilicate-water interface. In P. A. Oday, D. Vlassopoulos, Z. Meng & L. G. Benning (Eds.), *Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation* (Vol. 915, pp. 41-+). Washington: Amer Chemical Soc.

Chau, N. D., Dulinski, M., Jodlowski, P., Nowak, J., Rozanski, K., Sleziak, M., and Wachniew, P. (2011). Natural radioactivity in groundwater - a review. *Isotopes in Environmental and Health Studies, 47*(4), 415-437.

Chen, G. X., Liu, X. Y., and Su, C. M. (2012). Distinct Effects of Humic Acid on Transport and Retention of TiO2 Rutile Nanoparticles in Saturated Sand Columns. *Environmental Science & Technology, 46*(13), 7142-7150.

Chen, J., Meyerhof, D. P., and Tracy, B. L. (2004). Model results of kidney burdens from uranium intakes. *Health Physics, 86*(1), 3-11.

Chen, J. P., and Yiacoumi, S. (2002). Modeling of depleted uranium transport in subsurface systems. *Water Air and Soil Pollution, 140*(1-4), 173-201.

Chen, Z. R., Cai, Y., Liu, G. L., Solo-Gabriele, H., Snyder, G. H., and Cisar, J. L. (2008). Role of soil-derived dissolved substances in arsenic transport and transformation in laboratory experiments. *Science of the Total Environment, 406*(1-2), 180-189.

Cheng, H. F., Hu, Y. N., Luo, J., Xu, B., and Zhao, J. F. (2009). Geochemical processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems. *Journal of Hazardous Materials, 165*(1-3), 13-26.

Cheng, T., Barnett, M. O., Roden, E. E., and Zhuang, J. L. (2004). Effects of phosphate on uranium(VI) adsorption to goethite-coated sand. *Environmental Science & Technology, 38*(22), 6059-6065.

Cheng, T., Barnett, M. O., Roden, E. E., and Zhunag, J. L. (2007). Reactive transport of uranium(VI) and phosphate in a goethite-coated sand column: An experimental study. *Chemosphere, 68*(7), 1218-1223.

Chisholm-Brause, C. J., Berg, J. M., Little, K. M., Matzner, R. A., and Morris, D. E. (2004). Uranyl sorption by smectites: spectroscopic assessment of thermodynamic modeling. *Journal of Colloid and Interface Science, 277*(2), 366-382.

Cohen, S. M., Arnold, L. L., Eldan, M., Lewis, A. S., and Beck, B. D. (2006). Methylated arsenicals: The implications of metabolism and carcinogenicity studies in rodents to human risk assessment. *Critical Reviews in Toxicology, 36*(2), 99-133.

Cornu, S., Saada, A., Breeze, D., Gauthier, S., and Baranger, P. (1999). The influence of organic complexes on arsenic adsorption onto kaolinites. *Comptes Rendus De L Academie Des Sciences Serie Ii Fascicule a-Sciences De La Terre Et Des Planetes, 328*(10), 649-654.

Crancon, P., Pili, E., and Charlet, L. (2010). Uranium facilitated transport by water-dispersible colloids in field and soil columns. *Science of the Total Environment, 408*(9), 2118-2128.

Darland, J. E., and Inskeep, W. P. (1997). Effects of pH and phosphate competition on the transport of arsenate. *Journal of Environmental Quality, 26*(4), 1133-1139.

Datta, A., Sanyal, S. K., and Saha, S. (2001). A study on natural and synthetic humic acids and their complexing ability towards cadmium. *Plant and Soil, 235*(1), 115-125.

Dobran, S., and Zagury, G. J. (2006). Arsenic speciation and mobilization in CCA-contaminated soils: Influence of organic matter content. *Science of the Total Environment, 364*(1-3), 239-250.

Dodge, C. J., Francis, A. J., Gillow, J. B., Halada, G. P., Eng, C., and Clayton, C. R. (2002). Association of Uranium with Iron Oxides Typically Formed on

Corroding Steel Surfaces. *Environmental Science & Technology, 36*(16), 3504-3511.

Dresel, P. E., Wellman, D. M., Cantrell, K. J., and Truex, M. J. (2011). Review: Technical and Policy Challenges in Deep Vadose Zone Remediation of Metals and Radionuclides. *Environmental Science & Technology, 45*(10), 4207-4216.

Duff, M. C., Hunter, D. B., Bertsch, P. M., and Amrhein, C. (1999). Factors influencing uranium reduction and solubility in evaporation pond sediments. *Biogeochemistry, 45*(1), 95-114.

Fairhurst, A. J., Warwick, P., and Richardson, S. (1995). The influence of humic acid on the adsorption of europium onto inorganic colloids as a function of pH. *Colloids and Surfaces a-Physicochemical and Engineering Aspects, 99*(2-3), 187-199.

Fein, J. B., Boily, J.-F., Güçlü, K., and Kaulbach, E. (1999). Experimental study of humic acid adsorption onto bacteria and Al-oxide mineral surfaces. *Chemical Geology, 162*(1), 33-45.

Feng, X., Simpson, A. J., and Simpson, M. J. (2005). Chemical and mineralogical controls on humic acid sorption to clay mineral surfaces. *Organic Geochemistry, 36*(11), 1553-1566.

Filip, Z., and Alberts, J. J. (1994). Adsorption and transformation of salt marsh related humic acids by quartz and clay minerals. *Science of the Total Environment, 153*(1–2), 141-150.

Fox, P. M., Davis, J. A., and Zachara, J. M. (2006). The effect of calcium on aqueous uranium(VI) speciation and adsorption to ferrihydrite and quartz. *Geochimica Et Cosmochimica Acta, 70*(6), 1379-1387.

Gabriel, U., Gaudet, J. P., Spadini, L., and Charlet, L. (1998). Reactive transport of uranyl in a goethite column: an experimental and modelling study. *Chemical Geology, 151*(1-4), 107-128.

Gao, X. B., Wang, Y. X., Hu, Q. H., and Su, C. L. (2011). Effects of anion competitive adsorption on arsenic enrichment in groundwater. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering, 46*(5), 471-479.

Ghosh, A., Mukiibi, M., S áez, A. E., and Ela, W. P. (2006). Leaching of arsenic from granular ferric hydroxide residuals under mature landfill conditions. *Environmental Science and Technology, 40*(19), 6070-6075.

Giasuddin, A. B. M., Kanel, S. R., and Choi, H. (2007). Adsorption of humic acid onto nanoscale zerovalent iron and its effect on arsenic removal. *Environmental Science & Technology, 41*(6), 2022-2027.

Goldberg, S. (2002). Competitive Adsorption of Arsenate and Arsenite on Oxides and Clay Minerals. *Soil Science Society of America Journal, 66*(2), 413-421.

Gradusov, B. P. (1974). A tentative study of clay mineral distribution in soils of the world. *Geoderma, 12*(1–2), 49-55.

Greenland, D. J. (1971). Interactions between humic and fulvic acids and clays. *Soil*

Science, 111(1), 34-&.

Grolimund, D., Borkovec, M., Barmettler, K., and Sticher, H. (1996). Colloid-facilitated transport of strongly sorbing contaminants in natural porous media: A laboratory column study. *Environmental Science & Technology, 30*(10), 3118-3123.

Gu, B. H., Schmitt, J., Chen, Z. H., Liang, L. Y., and McCarthy, J. F. (1994). Adsorption and desorption of natural organic matter on iron-oxide: mechanisms and models. *Environmental Science & Technology, 28*(1), 38-46.

Gu, X., and Evans, L. J. (2007). Modelling the adsorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) onto Fithian illite. *Journal of Colloid and Interface Science, 307*(2), 317-325.

Guo, H. M., Zhang, B., Yang, S. Z., Li, Y., Stuben, D., Norra, S., and Wang, J. J. (2009). Role of colloidal particles for hydrogeochemistry in As-affected aquifers of the Hetao Basin, Inner Mongolia. *Geochemical Journal, 43*(4), 227-234.

Guo, H. M., Zhang, B., and Zhang, Y. (2011). Control of organic and iron colloids on arsenic partition and transport in high arsenic groundwaters in the Hetao basin, Inner Mongolia. *Applied Geochemistry, 26*(3), 360-370.

Halter, W. E., and Pfeifer, H.-R. (2001). Arsenic(V) adsorption onto α-Al2O3 between 25 and 70 ℃. *Applied Geochemistry, 16*(7–8), 793-802.

Haque, S., and Johannesson, K. H. (2006). Arsenic concentrations and speciation

along a groundwater flow path: The Carrizo Sand aquifer, Texas, USA. *Chemical Geology, 228*(1–3), 57-71.

Health Canada. (2006). Guidelines for Canadian Drinking Water Quality: Guideline Technical Document - Arsenic.

Health Canada. (2009). Guidelines for Canadian Drinking Water Quality: Guideline Technical Document - Radiological Parameters.

Hossain, M. S., and Islam, M. R. (2008). Experimental and numerical modeling of arsenic transport in limestone. *Energy Sources Part a-Recovery Utilization and Environmental Effects, 30*(13), 1189-1201.

Hsi, C. K. D., and Langmuir, D. (1985). Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochimica Et Cosmochimica Acta, 49*(9), 1931-1941.

Hu, L. G., Diez-Rivas, C., Hasan, A. R., Solo-Gabriele, H., Fieber, L., and Cai, Y. (2010). Transport and interaction of arsenic, chromium, and copper associated with CCA-treated wood in columns of sand and sand amended with peat. *Chemosphere, 78*(8), 989-995.

Hu, S. P., Chen, X. C., Shi, J. Y., Chen, Y. X., and Lin, Q. (2008). Particle-facilitated lead and arsenic transport in abandoned mine sites soil influenced by simulated acid rain. *Chemosphere, 71*(11), 2091-2097.

Ishak, C. F., Seaman, J. C., Miller, W. P., and Sumner, M. (2002). Contaminant mobility in soils amended with fly ash and flue-gas gypsum: Intact soil cores

and repacked columns. *Water, Air, and Soil Pollution, 134*(1-4), 287-305.

Ivanovich, M., and Harmon, R. S. (1992). *Uranium-series disequilibrium: Applications to earth, marine, and environmental sciences*: Oxford University Press.

Jada, A., Ait Akbour, R., and Douch, J. (2006). Surface charge and adsorption from water onto quartz sand of humic acid. *Chemosphere, 64*(8), 1287-1295.

Jerden Jr, J. L., and Sinha, A. K. (2006). Geochemical coupling of uranium and phosphorous in soils overlying an unmined uranium deposit: Coles Hill, Virginia. *Journal of Geochemical Exploration, 91*(1–3), 56-70.

Johnson, P. R., Sun, N., and Elimelech, M. (1996). Colloid transport in geochemically heterogeneous porous media: Modeling and measurements. *Environmental Science & Technology, 30*(11), 3284-3293.

Jomova, K., Jenisova, Z., Feszterova, M., Baros, S., Liska, J., Hudecova, D., Rhodes, C. J., and Valko, M. (2011). Arsenic: toxicity, oxidative stress and human disease. *Journal of Applied Toxicology, 31*(2), 95-107.

Kalbitz, K., and Wennrich, R. (1998). Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *Science of the Total Environment, 209*(1), 27-39.

Kaplan, D. I., Bertsch, P. M., Adriano, D. C., and Orlandini, K. A. (1994). Actinide association with groundwater colloids in a coastal-plain aquifer. *Radiochimica Acta, 66-7*, 181-187.

Kim, J. I., Delakowitz, B., Zeh, P., Klotz, D., and Lazik, D. (1994). A column experiment for the study of colloidal radionuclide migration in Gorleben aquifer systems. *Radiochimica Acta, 66-7*, 165-171.

Ko, I., Kim, J.-Y., and Kim, K.-W. (2004). Arsenic speciation and sorption kinetics in the As–hematite–humic acid system. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 234*(1–3), 43-50.

Kornilovich, B., Pshinko, G., Spasenova, L., and Kovalchuk, I. (2000). Influence of humic substances on the sorption interactions between lanthanide and actinide ions and clay minerals. *Adsorption Science & Technology, 18*(10), 873-880.

Kosmulski, M. (2011). The pH-dependent surface charging and points of zero charge: V. Update. *Journal of Colloid and Interface Science, 353*(1), 1-15.

Kostic, I., Andelkovic, T., Nikolic, R., Bojic, A., Purenovic, M., Blagojevic, S., and Andelkovic, D. (2011). Copper(II) and lead(II) complexation by humic acid and humic-like ligands. *Journal of the Serbian Chemical Society, 76*(9), 1325-1336.

Krepelova, A., Sachs, S., and Bernhard, G. (2006). Uranium(VI) sorption onto kaolinite in the presence and absence of humic acid. *Radiochimica Acta, 94*(12), 825-833.

Kretzschmar, R., Borkovec, M., Grolimund, D., and Elimelech, M. (1999). Mobile subsurface colloids and their role in contaminant transport. *Advances in Agronomy, Vol 66, 66*, 121-193.

Kretzschmar, R., and Schafer, T. (2005). Metal retention and transport on colloidal particles in the environment. *Elements, 1*(4), 205.

Kronfeld, J., Godfrey-Smith, D. I., Johannessen, D., and Zentilli, M. (2004). Uranium series isotopes in the Avon Valley, Nova Scotia. *Journal of Environmental Radioactivity, 73*(3), 335-352.

Kubicki, J. D., Schroeter, L. M., Itoh, M. J., Nguyen, B. N., and Apitz, S. E. (1999). Attenuated total reflectance Fourier-transform infrared spectroscopy of carboxylic acids adsorbed onto mineral surfaces. *Geochimica Et Cosmochimica Acta, 63*(18), 2709-2725.

Kurttio, P., Auvinen, A., Salonen, L., Saha, H., Pekkanen, J., Makelainen, I., Vaisanen, S. B., Penttila, I. M., and Komulainen, H. (2002). Renal effects of uranium in drinking water. *Environmental Health Perspectives, 110*(4), 337-342.

Kurttio, P., Harmoinen, A., Saha, H., Salonen, L., Karpas, Z., Komulainen, H., and Auvinen, A. (2006). Kidney toxicity of ingested uranium from drinking water. *American Journal of Kidney Diseases, 47*(6), 972-982.

Laegdsmand, M., de Jonge, L. W., and Moldrup, P. (2005). Leaching of colloids and dissolved organic matter from columns packed with natural soil aggregates. *Soil Science, 170*(1), 13-27.

Lenhart, J. J., Cabaniss, S. E., MacCarthy, P., and Honeyman, B. D. (2000). Uranium (VI) complexation with citric, humic and fulvic acids. *Radiochimica Acta, 88*(6/2000), 345.

Lenhart, J. J., and Honeyman, B. D. (1999). Uranium(VI) sorption to hematite in the presence of humic acid. *Geochimica Et Cosmochimica Acta, 63*(19–20), 2891-2901.

Li, W. C., Victor, D. M., and Chakrabarti, C. L. (1980). Effect of pH and uranium concentration on interaction of uranium (VI) and uranium (IV) with organic ligands in aqueous solutions. *Analytical chemistry, 52*(3), 520-523.

Li, X., Wu, J., Liao, J., Zhang, D., Yang, J., Feng, Y., Zeng, J., Wen, W., Yang, Y., Tang, J., and Liu, N. (2013). Adsorption and desorption of uranium (VI) in aerated zone soil. *Journal of Environmental Radioactivity, 115*(0), 143-150.

Lienert, C., Short, S. A., and Vongunten, H. R. (1994). Uranium infiltration from a river to shallow groundwater. *Geochimica Et Cosmochimica Acta, 58*(24), 5455-5463.

Lin, Z., and Puls, R. W. (2000). Adsorption, desorption and oxidation of arsenic affected by clay minerals and aging process. *Environmental Geology, 39*(7), 753-759.

Lippold, H., and Lippmann-Pipke, J. (2009). Effect of humic matter on metal adsorption onto clay materials: Testing the linear additive model. *Journal of Contaminant Hydrology, 109*(1–4), 40-48.

Liu, A. G., and Gonzalez, R. D. (1999). Adsorption/desorption in a system consisting of humic acid, heavy metals, and clay minerals. *Journal of Colloid and Interface Science, 218*(1), 225-232.

Maity, J. P., Nath, B., Chen, C. Y., Bhattacharya, P., Sracek, O., Bundschuh, J., Kar, S., Thunvik, R., Chatterjee, D., Ahmed, K. M., Jacks, G., Mukherjee, A. B., and Jean, J. S. (2011). Arsenic-enriched groundwaters of India, Bangladesh and Taiwan-Comparison of hydrochemical characteristics and mobility constraints. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering*, *46*(11), 1163-1176.

Mamindy-Pajany, Y., Hurel, C., Marmier, N., and Roméo, M. (2011). Arsenic (V) adsorption from aqueous solution onto goethite, hematite, magnetite and zero-valent iron: Effects of pH, concentration and reversibility. *Desalination, 281*(0), 93-99.

Mandal, B. K., and Suzuki, K. T. (2002). Arsenic round the world: a review. *Talanta, 58*(1), 201-235.

Manning, B. A., and Goldberg, S. (1997). Adsorption and stability of arsenic(III) at the clay mineral-water interface. *Environmental Science & Technology, 31*(7), 2005-2011.

McCarthy, J. F., and McKay, L. D. (2004). Colloid mobilization and transport in groundwater. *Vadose Zone Journal, 3*(2), 326-337.

McKinley, J. P., Zachara, J. M., Smith, S. C., and Turner, G. D. (1995). The influence of uranyl hydrolysis and multiple site-binding reactions on adsorption of U(VI) to montmorillonite. *Clays and Clay Minerals, 43*(5), 586-598.

Metreveli, G., Abbt-Braun, G., and Frimmel, F. H. (2010). Influence of NOM on the

Mobility of Metal(loid)s in Water-Saturated Porous Media. *Aquatic Geochemistry, 16*(1), 85-100.

Mibus, J., Sachs, S., Pfingsten, W., Nebelung, C., and Bernhard, G. (2007). Migration of uranium(IV)/(VI) in the presence of humic acids in quartz sand: A laboratory column study. *Journal of Contaminant Hydrology, 89*(3-4), 199-217.

Missana, T., Garcia-Gutierrez, M., and Alonso, U. (2004). Kinetics and irreversibility of cesium and uranium sorption onto bentonite colloids in a deep granitic environment. *Applied Clay Science, 26*(1-4), 137-150.

Mohapatra, D., Mishra, D., Chaudhury, G. R., and Das, R. P. (2007). Arsenic(V) adsorption mechanism using kaolinite, montmorillonite and illite from aqueous medium. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering, 42*(4), 463-469.

Morales, V. L., Zhang, W., Gao, B., Lion, L. W., Bisogni, J. J., McDonough, B. A., and Steenhuis, T. S. (2011). Impact of dissolved organic matter on colloid transport in the vadose zone: Deterministic approximation of transport deposition coefficients from polymeric coating characteristics. *Water Research, 45*(4), 1691-1701.

Moyes, L. N., Parkman, R. H., Charnock, J. M., Vaughan, D. J., Livens, F. R., Hughes, C. R., and Braithwaite, A. (2000). Uranium Uptake from Aqueous Solution by Interaction with Goethite, Lepidocrocite, Muscovite, and Mackinawite: An

X-ray Absorption Spectroscopy Study. *Environmental Science & Technology, 34*(6), 1062-1068.

Paktunc, D., Foster, A., and Laflamme, G. (2003). Speciation and characterization of arsenic in Ketza River mine tailings using x-ray absorption spectroscopy. *Environmental Science & Technology, 37*(10), 2067-2074.

Patel, K. S., Shrivas, K., Brandt, R., Jakubowski, N., Corns, W., and Hoffmann, P. (2005). Arsenic contamination in water, soil, sediment and rice of central India. *Environmental Geochemistry and Health, 27*(2), 131-145.

Payne, T. E., Davis, J. A., and Waite, T. D. (1996). Uranium adsorption on ferrihydrite - Effects of phosphate and humic acid. *Radiochimica Acta, 74*, 239-243.

Pitois, A., Abrahamsen, L. G., Ivanov, P. I., and Bryan, N. D. (2008). Humic acid sorption onto a quartz sand surface: A kinetic study and insight into fractionation. *Journal of Colloid and Interface Science, 325*(1), 93-100.

Plaschke, M., Romer, J., Klenze, R., and Kim, J. I. (1999). In situ AFM study of sorbed humic acid colloids at different pH. *Colloids and Surfaces a-Physicochemical and Engineering Aspects, 160*(3), 269-279.

Polubesova, T., and Nir, S. (1999). Modeling of organic and inorganic cation sorption by illite. *Clays and Clay Minerals, 47*(3), 366-374.

Prikryl, J. D., Jain, A., Turner, D. R., and Pabalan, R. T. (2001a). Uranium(VI) sorption behavior on silicate mineral mixtures. *Journal of Contaminant Hydrology, 47*(2-4), 241-253.

Prikryl, J. D., Jain, A., Turner, D. R., and Pabalan, R. T. (2001b). UraniumVI sorption behavior on silicate mineral mixtures. *Journal of Contaminant Hydrology, 47*(2–4), 241-253.

Puls, R. W., and Powell, R. M. (1992). Transport of inorganic colloids through natural aquifer material: Implications for contaminant transport. *Environmental Science and Technology, 26*(3), 614-621.

Radu, T., Subacz, J. L., Phillippi, J. M., and Barnett, M. O. (2005). Effects of dissolved carbonate on arsenic adsorption and mobility. *Environmental Science & Technology, 39*(20), 7875-7882.

Ransom, B., and Helgeson, H. C. (1993). Compositional end members and thremodynamic components of illite and dioctahedral aluminous smectite solid-solutions. *Clays and Clay Minerals, 41*(5), 537-550.

Raven, K. P., Jain, A., and Loeppert, R. H. (1998). Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. *Environmental Science & Technology, 32*(3), 344-349.

Redman, A. D., Macalady, D. L., and Ahmann, D. (2002). Natural organic matter affects arsenic speciation and sorption onto hematite. *Environmental Science & Technology, 36*(13), 2889-2896.

Reich, T., Moll, H., Arnold, T., Denecke, M. A., Hennig, C., Geipel, G., Bernhard, G., Nitsche, H., Allen, P. G., Bucher, J. J., Edelstein, N. M., and Shuh, D. K. (1998). An EXAFS study of uranium(VI) sorption onto silica gel and

ferrihydrite. *Journal of Electron Spectroscopy and Related Phenomena, 96*(1–3), 237-243.

Ribera, D., Labrot, F., Tisnerat, G., and Narbonne, J. F. (1996). Uranium in the environment: occurrence, transfer, and biological effects. *Reviews of environmental contamination and toxicology, 146*, 53.

Sachs, S., and Bernhard, G. (2008). Sorption of U(VI) onto an artificial humic substance-kaolinite-associate. *Chemosphere, 72*(10), 1441-1447.

Sachs, S., Geipel, G., Mibus, J., and Bernhard, G. (2006). Impact of humic acid on the uranium migration in the environment

Uranium in the Environment. In B. J. Merkel & A. Hasche-Berger (Eds.), (pp. 107-116): Springer Berlin Heidelberg.

Saiers, J. E. (2002). Laboratory observations and mathematical modeling of colloid-facilitated contaminant transport in chemically heterogeneous systems. *Water Resources Research, 38*(4).

Saiers, J. E., and Hornberger, G. M. (1999). The influence of ionic strength on the facilitated transport of cesium by kaolinite colloids. *Water Resources Research, 35*(6), 1713-1727.

Schmeide, K., Pompe, S., Bubner, M., Heise, K. H., Bernhard, G., and Nitsche, H. (2000). Uranium(VI) sorption onto phyllite and selected minerals in the presence of humic acid. *Radiochimica Acta, 88*(9-11), 723-728.

Schmitt, D., Saravia, F., Frimmel, F. H., and Schuessler, W. (2003). NOM-facilitated

transport of metal ions in aquifers: importance of complex-dissociation kinetics and colloid formation. *Water Research, 37*(15), 3541-3550.

Serpa, C., Batterson, M. and Guzzwell, K. . (2009). The influence of bedrock and mineral occurrences on Arsenic concentrations in groundwater wells in the Gander Bay Area, Newfoundland. *Current Research (2009) Newfoundland and Labrador Department of Natural Resources Geological Survey*(Report 09-1), 315-337.

Sharma, P., and Kappler, A. (2011). Desorption of arsenic from clay and humic acid-coated clay by dissolved phosphate and silicate. *Journal of Contaminant Hydrology, 126*(3-4), 216-225.

Sharma, P., Rolle, M., Kocar, B., Fendorf, S., and Kappler, A. (2011). Influence of Natural Organic Matter on As Transport and Retention. *Environmental Science & Technology, 45*(2), 546-553.

Shuibo, X., Chun, Z., Xinghuo, Z., Jing, Y., Xiaojian, Z., and Jingsong, W. (2009). Removal of uranium (VI) from aqueous solution by adsorption of hematite. *Journal of Environmental Radioactivity, 100*(2), 162-166.

Slowey, A. J., Johnson, S. B., Newville, M., and Brown Jr, G. E. (2007). Speciation and colloid transport of arsenic from mine tailings. *Applied Geochemistry, 22*(9), 1884-1898.

Smedley, P. L., and Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry, 17*(5),

517-568.

Su, T. Z., Guan, X. H., Gu, G. W., and Wang, J. M. (2008). Adsorption characteristics of As(V), Se(IV), and V(V) onto activated alumina: Effects of pH, surface loading, and ionic strength. *Journal of Colloid and Interface Science, 326*(2), 347-353.

Tang, X. Y., and Weisbrod, N. (2009). Colloid-facilitated transport of lead in natural discrete fractures. *Environmental Pollution, 157*(8-9), 2266-2274.

Tatalovich, M. E., Lee, K. Y., and Chrysikopoulos, C. V. (2000). Modeling the transport of contaminants originating from the dissolution of DNAPL pools in aquifers in the presence of dissolved humic substances. *Transport in Porous Media, 38*(1-2), 93-115.

Tessema, D. A., and Kosmus, W. (2001). Influence of humic and low molecular weight polycarboxylic acids on the release of arsenic from soils. *Journal of Trace and Microprobe Techniques, 19*(2), 267-278.

Tessier, A., Campbell, P. G., and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical chemistry, 51*(7), 844-851.

Tindale, K., Patel, P., and Wallschlager, D. (2011). Colloidal arsenic composition from abandoned gold mine tailing leachates in Nova Scotia, Canada. *Applied Geochemistry, 26*, S260-S262.

Tipping, E. (1981). The adsorption of aquatic humic substances by iron oxides.

Geochimica Et Cosmochimica Acta, *45*(2), 191-199.

Tombacz, E., Dobos, A., Szekeres, M., Narres, H. D., Klumpp, E., and Dekany, I. (2000). Effect of pH and ionic strength on the interaction of humic acid with aluminium oxide. *Colloid and Polymer Science*, *278*(4), 337-345.

Tufano, K. J., and Fendorf, S. (2008). Confounding impacts of iron reduction on arsenic retention. *Environmental Science & Technology, 42*(13), 4777-4783.

Waite, T. D., Davis, J. A., Payne, T. E., Waychunas, G. A., and Xu, N. (1994). Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. *Geochimica Et Cosmochimica Acta, 58*(24), 5465-5478.

Walter, M., Arnold, T., Geipel, G., Scheinost, A., and Bernhard, G. (2005). An EXAFS and TRLFS investigation on uranium(VI) sorption to pristine and leached albite surfaces. *Journal of Colloid and Interface Science, 282*(2), 293-305.

Walter, M., Arnold, T., Reich, T., and Bernhard, G. (2003). Sorption of Uranium(VI) onto Ferric Oxides in Sulfate-Rich Acid Waters. *Environmental Science & Technology, 37*(13), 2898-2904.

Wang, S., and Mulligan, C. N. (2006). Occurrence of arsenic contamination in Canada: Sources, behavior and distribution. *Science of the Total Environment, 366*(2-3), 701-721.

Wang, S. L., and Mulligan, C. N. (2009a). Effect of natural organic matter on arsenic mobilization from mine tailings. *Journal of Hazardous Materials, 168*(2-3), 721-726.

Wang, S. L., and Mulligan, C. N. (2009b). Enhanced mobilization of arsenic and heavy metals from mine tailings by humic acid. *Chemosphere, 74*(2), 274-279.

Wang, T., Liu, W., Xiong, L., Xu, N., and Ni, J. R. (2013). Influence of pH, ionic strength and humic acid on competitive adsorption of Pb(II), Cd(II) and Cr(III) onto titanate nanotubes. *Chemical Engineering Journal, 215*, 366-374.

Wazne, M., Korfiatis, G. P., and Meng, X. (2003). Carbonate Effects on Hexavalent Uranium Adsorption by Iron Oxyhydroxide. *Environmental Science & Technology, 37*(16), 3619-3624.

Williams, L. E., Barnett, M. O., Kramer, T. A., and Melville, J. G. (2003). Adsorption and transport of arsenic(V) in experimental subsurface systems. *Journal of Environmental Quality, 32*(3), 841-850.

Xu, H., Allard, B., and Grimvall, A. (1988). Influence of pH and organic substance on the adsorption of As(V) on geologic materials. *Water, Air, and Soil Pollution, 40*(3-4), 293-305.

Xu, H., Allard, B., and Grimvall, A. (1991). Effects of acidification and natural organic materials on the mobility of arsenic in the environment. *Water Air and Soil Pollution, 57-8*, 269-278.

Yang, Y., Saiers, J. E., and Barnett, M. O. (2013). Impact of Interactions between Natural Organic Matter and Metal Oxides on the Desorption Kinetics of Uranium from Heterogeneous Colloidal Suspensions. *Environmental Science & Technology, 47*(6), 2661-2669.

Yang, Y., Saiers, J. E., Xu, N., Minasian, S. G., Tyliszczak, T., Kozimor, S. A., Shuh, D. K., and Barnett, M. O. (2012). Impact of Natural Organic Matter on Uranium Transport through Saturated Geologic Materials: From Molecular to Column Scale. *Environmental Science & Technology, 46*(11), 5931-5938.

Yolcubal, I., and Akyol, N. H. (2008). Adsorption and transport of arsenate in carbonate-rich soils: Coupled effects of nonlinear and rate-limited sorption. *Chemosphere, 73*(8), 1300-1307.

Yoshida, T., and Suzuki, M. (2008). Effects of humic acid on migration of montmorillonite and alumina colloid in a quartz sand column. *Colloids and Surfaces a-Physicochemical and Engineering Aspects, 325*(3), 115-119.

Zamora, M. L., Tracy, B. L., Zielinski, J. M., Meyerhof, D. P., and Moss, M. A. (1998). Chronic ingestion of uranium in drinking water: A study of kidney bioeffects in humans. *Toxicological Sciences, 43*(1), 68-77.

Zhang, H., and Selim, H. M. (2007). Colloid mobilization and arsenite transport in soil columns: Effect of ionic strength. *Journal of Environmental Quality, 36*(5), 1273-1280.

Zhang, L., Yu, X., Zhang, H., Chen, E., and Dong, T. (2013). Impact of environmental conditions on the sorption behavior of 60Co(II) on illite. *Journal of Radioanalytical and Nuclear Chemistry, 295*(2), 1473-1485.

Zhang, W., Morales, V. L., Cakmak, M. E., Salvucci, A. E., Geohring, L. D., Hay, A. G., Parlange, J. Y., and Steenhuis, T. S. (2010). Colloid Transport and

Retention in Unsaturated Porous Media: Effect of Colloid Input Concentration. *Environmental Science & Technology, 44*(13), 4965-4972.